



Silicon regulation of soil organic carbon stabilization and its potential to mitigate climate change

Zhaoliang Song^{a,*}, Congqiang Liu^a, Karin Müller^b, Xiaomin Yang^a, Yuntao Wu^a, Hailong Wang^{c,d,*}

^a Institute of Surface-Earth System Science, Tianjin University, Tianjin 300072, China

^b The New Zealand Institute for Plant & Food Research Limited, Ruakura Research Centre, Private Bag 3230, Waikato Mail Centre, Hamilton 3240, New Zealand

^c Key Laboratory of Soil Contamination Bioremediation of Zhejiang Province, School of Environmental & Resource Sciences, Zhejiang A & F University, Lin'an, Hangzhou, Zhejiang 311300, China

^d School of Environment and Chemical Engineering, Foshan University, Foshan, Guangdong 528000, China

ARTICLE INFO

Keywords:

Biogeochemical silicon cycle
Phytolith
Secondary mineral
Soil organic carbon
Stabilization
Terrestrial ecosystem

ABSTRACT

The terrestrial biogeochemical silicon (Si) cycle may significantly influence the stabilization of soil organic carbon (SOC), and thus plays an important role in regulating the global carbon (C) balance and climate change. Processes involved in Si-enhanced SOC stability at a decadal or centennial scale include protection of SOC through amorphous Si and interactions of Si-iron and Si-aluminum. Strategic manipulation of the Si cycle in terrestrial ecosystems offers a new opportunity to enhance soil C sequestration. Rock powder amendment, establishment of Si-rich plant buffer strips and innovative management practices that return Si-rich biomass materials to soil can be implemented as strategies to enhance soil C sequestration through regulating the terrestrial Si cycle. However, quantifying (i) the contribution of different processes to the enhancement of soil dissolved Si and secondary Si minerals, (ii) the relative importance of different SOC stabilization mechanisms, and (iii) the potential and cost of different measures has not been attempted.

1. Introduction

The biogeochemical carbon (C) cycle and its coupling with nutrients such as nitrogen (N) in terrestrial ecosystems and in oceans play important roles in regulating global climate change (Falkowski et al., 2000; Gao et al., 2016; Yu et al., 2016). Soil is the largest active pool in the terrestrial C cycle (Schmidt et al., 2011; Lehmann and Kleber, 2015) and stores 1220 to 4800 Pg (1 Pg = 10^{15} g) organic C globally (Jobbágy and Jackson, 2000; Lehmann and Kleber, 2015). It has been frequently reported that the majority of soil organic carbon (SOC) decomposes readily within several years while a minority of SOC persists for several millennia (Sulman et al., 2014; Keiluweit et al., 2015; Hatté et al., 2017). As molecular structure alone cannot explain these differences in SOC stability (Schmidt et al., 2011), many other SOC stabilization mechanisms including physico-chemical protection of SOC by micro- and macro- aggregates (Jastrow et al., 2007; O'Rourke et al., 2015), spatial inaccessibility of SOC against decomposer due to encapsulation, occlusion and hydrophobicity (von Lützow et al., 2006; Rumpel et al., 2012) and mineral-organic associations (Mikutta et al., 2009; Schulze et al., 2009; Kleber et al., 2014) have been proposed. However, the

relative importance of each mechanism in controlling SOC stability at a decadal or centennial scale varies greatly with environmental conditions (Schmidt et al., 2011; O'Rourke et al., 2015), which prevents us from accurately predicting how SOC will respond to future climate change and ecosystem disturbance (Doetterl et al., 2015; Keiluweit et al., 2015).

Silicon (Si), an abundant beneficial element for plants to resist abiotic and biotic stresses (Fauteux et al., 2006; Ma et al., 2006; Ye et al., 2013), plays a more important role in controlling the long-term global C cycle than other nutrients (e.g., N) through complex interactions between Si and C cycles such as biogeochemical weathering of silicates (Song et al., 2011; Maher and Chamberlain, 2014; Taylor et al., 2015), diatom C sequestration (Smetacek et al., 2012; Bailleul et al., 2015; Cermeño et al., 2015) and phytolith C sequestration (Parr et al., 2010; Song et al., 2013, 2016). There is still controversy about the role of Si in straw/litter decomposition and methane emission (Ali et al., 2008; Clymans et al., 2016; Emsens et al., 2016; Marxen et al., 2016; Reithmaier et al., 2017) because of differences in environmental conditions (e.g., arid and submerged conditions) and experimental treatments (e.g., different Si sources and doses). However, recent studies

Abbreviations: Si, silicon; SOC, soil organic carbon; C, carbon; Fe, iron; Al, aluminum; BSi, biogenic Si; LASi, lithogenic amorphous Si; TSi, total Si; DSi, dissolved Si; MOA, mineral-organic associations

* Corresponding author at: Institute of Surface-Earth System Science, Tianjin University, NO. 92, Weijin Road, Tianjin 300072, China.

E-mail addresses: zhaoliang.song@tju.edu.cn (Z. Song), hailong.wang@fosu.edu.cn (H. Wang).

<https://doi.org/10.1016/j.earscirev.2018.06.020>

Received 23 October 2017; Received in revised form 22 June 2018; Accepted 29 June 2018

Available online 30 June 2018

0012-8252/ © 2018 Elsevier B.V. All rights reserved.

demonstrated the possibility of regulation of SOC stabilization by Si and its potential to mitigate climate change (Matus et al., 2014; Parr and Sullivan, 2014; Huang et al., 2016). For example, similar to some clays, biogenic Si (e.g., phytoliths) has a multi-porous structure with pore neck diameters $< 1 \mu\text{m}$ and a large specific area $92\text{--}316 \text{ m}^2 \text{ g}^{-1}$. It fills or closely adsorbs SOC in its cavities or loosely adsorbs SOC to its outer surfaces, which may decrease the exposure of SOC to microbes and enzymes, and thereby, stabilize SOC (Jastrow et al., 2007; Frayse et al., 2009; Parr and Sullivan, 2014). Furthermore, as iron (Fe), aluminum (Al) and SOC are the main components of mineral-organic associations (Mikutta et al., 2009) and aggregates (Mataix-Solera et al., 2011; Huang et al., 2016), the terrestrial biogeochemical Si cycle may also control the biogeochemical behaviors of Fe and Al in terrestrial ecosystems through feedbacks of Si–Fe (Pokrovski et al., 2003; Gauger et al., 2016) and Si–Al (Matus et al., 2014; Huang et al., 2016). This will in turn influence the stability of mineral-organic associations, aggregates and SOC.

Despite the importance of Si for SOC stabilization and the global biogeochemical C cycle, the interaction between SOC and biogenic Si should be investigated and quantified in more detail in future (Song et al., 2012b). This paper summarizes and reviews the terrestrial biogeochemical Si cycle and SOC stabilization with specific focus on the interactions between the Si cycle and SOC stability. We first introduce the terrestrial biogeochemical Si cycle, and then summarize sources and turnover of SOC in soil profiles plus SOC stabilization processes. Next, we briefly review direct and indirect evidence for the interactions between the Si cycle and SOC stability: (1) SOC protection by biogenic Si (e.g., phytolith, diatom, microbial and protozoic Si), (2) SOC stability regulated by interactions between Si and Fe, and (3) SOC stability regulated by interactions between Si and Al. Finally, we discuss the potential of different management strategies to regulate the Si cycle and thereby enhance soil C sequestration. We also identify knowledge gaps and suggest areas for possible future research.

2. Biogeochemical Si cycle in terrestrial ecosystems

Terrestrial ecosystems are reactors of the biogeochemical Si cycle in which, dissolved, mineralogical and biogenic Si pools undergo various processes of mobilization, immobilization and translocation on different time scales (Fig. 1).

2.1. Si pools in terrestrial ecosystems

Terrestrial Si pools consist of dissolved and solid phases (Conley, 2002; Sommer et al., 2006; Struyf et al., 2010). Dissolved Si is mainly derived from the weathering dissolution of silicates and other solid phases (Derry et al., 2005; Trembath-Reichert et al., 2015), and may be precipitated as mineralogical or biogenic Si (Fig. 1). Under most soil pH conditions ($2.5 < \text{pH} < 8.5$), dissolved Si ranges in concentration from 100 to $500 \mu\text{M}$ (Derry et al., 2005; Sommer et al., 2006) and consists mainly of monomeric orthosilicic acid (H_4SiO_4) (Dove, 1995; Matichenkov and Snyder, 1996).

The soil mineralogical Si pool consists of primary silicate minerals, clays, and poorly to non-crystalline phases (Matichenkov and Snyder, 1996; Basile-Doelsch et al., 2005). Primary silicate minerals are inherited from parent materials, whereas secondary components are formed during soil development (Matichenkov and Bocharnikova, 2001; Monger and Kelly, 2002). Amorphous and adsorbed Si are immediate sources or sinks of dissolved Si (Drees et al., 1989; Pokrovski et al., 2003).

Terrestrial biogenic Si consists of phytogenic, protozoic and microbial Si forms (Fig. 1) (Clarke, 2003; Aoki et al., 2007; Puppe et al., 2015). As a major biogenic Si pool, phytogenic Si is formed through the precipitation of dissolved Si to amorphous silica ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$) near the end of water transpiration in plants (e.g. stomata) (Piperno, 1988; Sommer et al., 2006; Dunn et al., 2015). Phytogenic Si includes

phytoliths ($\geq 5 \mu\text{m}$ Ø) usually with distinct shapes and undefined phytogenic Si ($< 5 \mu\text{m}$ Ø). Phytogenic Si storage in soils varies from 400 to $170,000 \text{ kg ha}^{-1}$, which is 500 to 1000 times larger than that in plants (Conley, 2002; Song et al., 2016).

2.2. Biological uptake and restitution of Si to soil

Plants can take up dissolved Si actively or passively with the water mass flow (Ma et al., 2001, 2006) and form phytogenic Si precipitation in plant tissues. Phytogenic Si content ranges from 0.1% to larger than 10% in different plant species (Epstein, 1994, 1999; Trembath-Reichert et al., 2015). Some plants (e.g., graminaceous plants) take up more Si from the soil solution than other plants and thus, have a larger effect on the Si cycle because of higher Si content and net primary production (Song et al., 2012a, 2013). Conley (2002) estimated that the phytogenic Si production rate in global terrestrial ecosystems ranges between 60 and $200 \text{ Tmole Si yr}^{-1}$.

Phytogenic Si in plants may be returned to soils through litterfall and accumulated in soils after litter decomposition. The soil accumulation of phytogenic Si depends not only on the return of phytogenic Si through litterfall but also on the phytogenic Si stability (Fig. 1) (Blecker et al., 2006; Frayse et al., 2006, 2009). The stability of phytogenic Si is not only affected by environmental conditions (e.g., climate, soil pH) but also controlled by phytogenic Si properties (e.g., specific surface area) (Bartoli and Wilding, 1980; Bartoli, 1985; Blecker et al., 2006).

2.3. Plant control on silicate weathering and accumulation of secondary minerals

Rates of silicate weathering depend not only on lithology and climatic conditions but also on biological activities (Lucas et al., 1993; Berner, 1997; Lucas, 2001). For example, plants can accelerate basalt weathering by 2 to 8-fold (Drever and Zobrist, 1992; Moulton et al., 2000) through plant and microbial interactions, altered soil physical properties and ion-exchange equilibria (Moulton and Berner, 1998; Hinsinger et al., 2001; Lucas, 2001; Song et al., 2012b).

The forming processes and properties of secondary minerals with different C stabilization potential (Baldock and Skjemstad, 2000; Kleber et al., 2014) differ in various weathering environments (Baldock and Skjemstad, 2000; Matus et al., 2014). For example, the wide formation and accumulation of kaolinite in the upper soil horizons of the humid tropics can only be maintained by the high biological activities of tropical ecosystems (Lucas et al., 1993).

2.4. Export of dissolved Si to watersheds

Watershed dissolved Si outputs vary from 0.1 to $8 \text{ kmol ha}^{-1} \text{ yr}^{-1}$ (Oliva et al., 1999; Turner et al., 2003) depending not only on runoff, temperature and lithology (White and Blum, 1995; Struyf et al., 2010) but also on plants (Fig. 1) (Derry et al., 2005; Sommer et al., 2006). For example, between 75% and 95% of the stream dissolved Si had passed through the biogenic Si pool in Hawaiian (Derry et al., 2005), which is usually coupled with the release of dissolved organic carbon (DOC) through biogenic Si dissolution (Lucas, 2001; Sommer et al., 2006).

2.5. Response of terrestrial Si balance to ecosystem disturbance

Anthropogenic activities such as changes in land use and land cover, biomass harvest, fertilization and organic mulching have significantly changed Si balance of terrestrial ecosystems (Conley et al., 2008; Meunier et al., 2008; Carey and Fulweiler, 2012; Vandevenne et al., 2012). For example, Struyf et al. (2010) found that continuous cultivation (> 250 years) of previously forested areas caused a 2 to 3-fold decrease in stream Si export, which is related to different deforestation stages (Fig. 2).

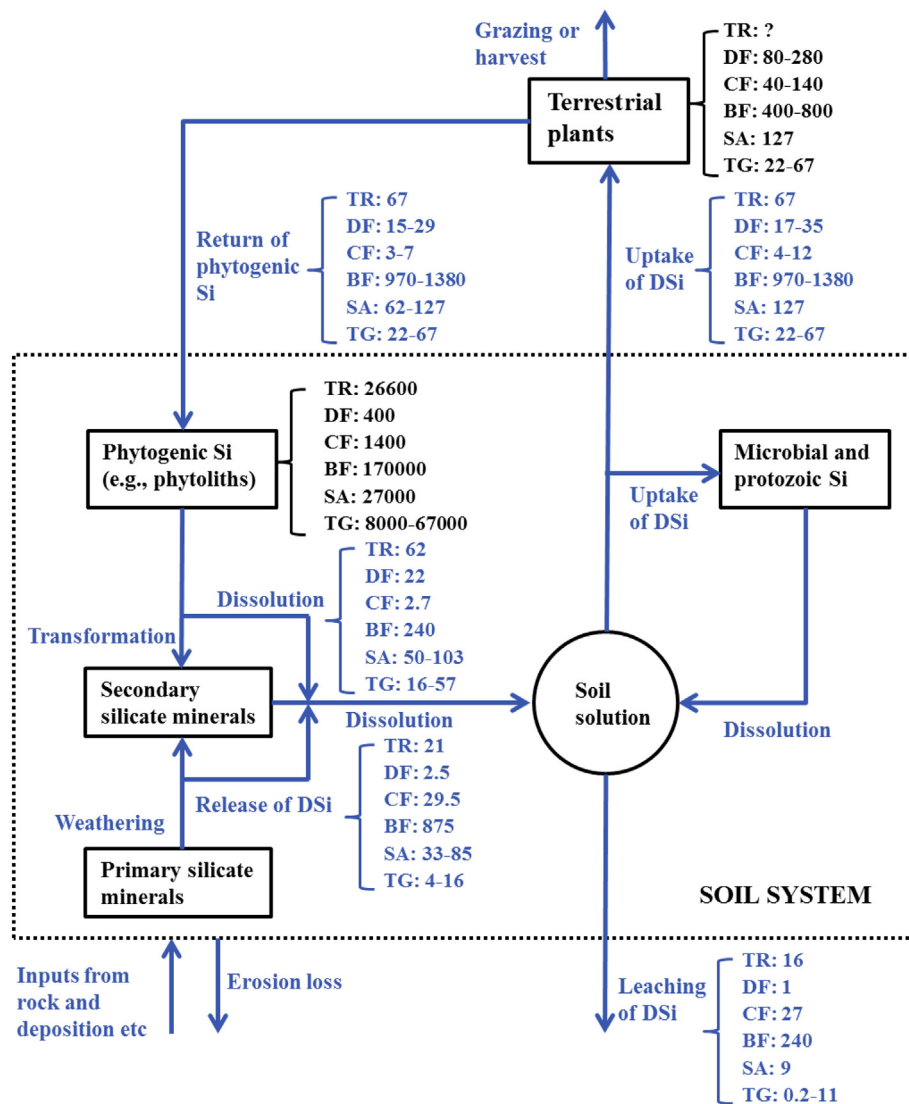


Fig. 1. Pools and fluxes of Si in terrestrial ecosystems. The Si pools are in black and its fluxes are in blue. TR, Tropical rainforest; DF, Deciduous forest; CF, Coniferous forest; BF, Bamboo forest; SA, Savanna; TG, Temperate grassland. Si pools and fluxes are expressed in kg ha^{-1} and $\text{kg ha}^{-1} \text{yr}^{-1}$, respectively. Data are from Alexandre et al. (1997, 2011), Conley (2002), Blecker et al. (2006), Sommer et al. (2006), Reyerson (2007), Struyf and Conley (2012), Umemura and Takenaka (2014). DSi = dissolved Si. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3. Turnover processes of SOC in soil profiles

SOC consists mainly of alkanolic acids, *n*-alkanes, lignins, plant lipids, sugars, proteins, and saccharides (Kleber and Johnson, 2010; Schmidt et al., 2011). The chemical nature of SOC associated with minerals in topsoils mainly reflects the composition of the vegetation source, while in subsoils, the contribution of different organic compounds may be affected not only by carbon sources (e.g., DOC and root products) (Rumpel and Kögel-Knabner, 2011; Austin et al., 2016) and microbial activities (Campbell and Paustian, 2015) but also by soil mineral composition due to selective protection of organic compounds by minerals (Mikutta et al., 2009).

3.1. Turnover time of organic C in soil profiles

Topsoil SOC stocks respond rapidly to management practices, land use and climate change (Lal, 2004a, 2004b; Machmuller et al., 2015). In soil profiles, SOC may form intricate associations with soil secondary minerals through myriad interactions (Kleber et al., 2014). However, the C content of mineral-organic associations and the percentage of mineral-organic associated C in total SOC vary significantly with soil

minerals and their formation conditions (Table 1; Schulze et al., 2009; Torn et al., 2013), which may be influenced by biogeochemical Si cycle (Lucas et al., 1993; Lucas, 2001; Song et al., 2014).

The turnover time of SOC depends not only on the molecular structure of SOC itself but also on abiotic and biotic conditions (Schmidt et al., 2011; Lehmann and Kleber, 2015; Hatté et al., 2017). It generally increases with soil depth and decreases with temperature and precipitation (Schulze et al., 2009; Sollins et al., 2009; Schmidt et al., 2011). The turnover time of mineral-organic associated C is generally longer than that of other SOC fractions despite its great variability (32 to 2170 years) with soil depth and soil formation conditions (Table 1).

3.2. SOC stabilization and destabilization

SOC may be stabilized through physical (e.g., aggregation and spatial separation from decomposers) and geochemical (mineral-organic association, sorption, complexation etc.) mechanisms (Kleber et al., 2014; Doetterl et al., 2016). Physical mechanisms of SOC stabilization have already been well studied (Baldock and Skjemstad, 2000; Six et al., 2002; Jastrow et al., 2007). In contrast, geochemical mechanisms such as mineral-organic association are less well investigated

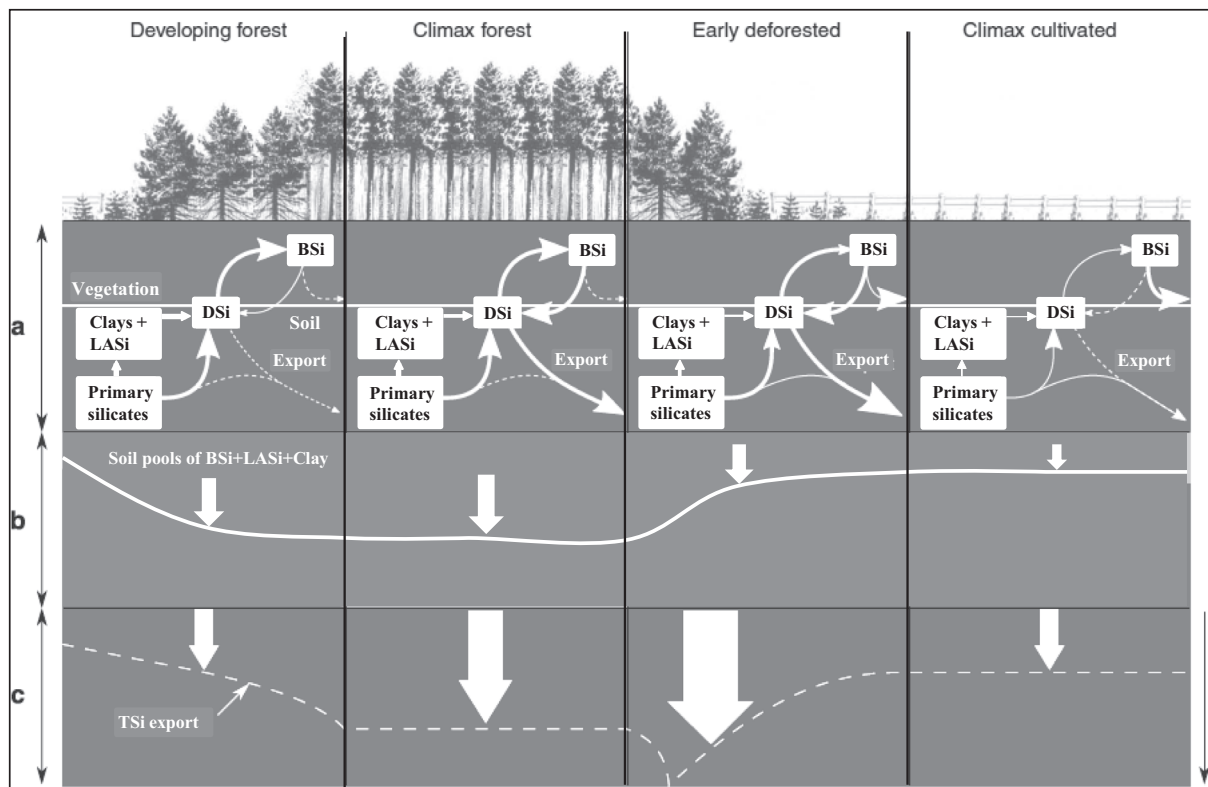


Fig. 2. Conceptual model for Si cycle changes with soil disturbance (modified from [Struyf et al., 2010](#)). (a) Si cycle in developing and climax forest, areas of early deforestation and climax cultivation. (b) Evolution of the combined soil stock of biogenic Si (BSi), lithogenic amorphous Si (LASi) and clays. (c) Evolution of export of total Si (TSi) including BSi, LASi and dissolved Si (DSi). Boxes represent Si stocks while arrows represent Si fluxes. The thickness of the arrows indicates flux size. Dashed arrows mean negligible fluxes.

Table 1

Storage and turnover time of soil organic carbon (SOC) in various soil fractions using density fractionation.

Ecosystem type	Soil properties	Density cutoff (g mL ⁻¹) ^a	Carbon storage		Carbon turnover (yr)		Data sources
			% C in MOA ^b	% MOA-C of SOC ^c	MOA-C	Other fractions	
Tropical forest	Inceptisol, 0–5 cm	2.0	11.0	54	71–295	60–73	Sollins et al. (2009)
Subtropical forest	Oxisol, 2–12 cm	2.0	6.5	76	107–400	81–93	Sollins et al. (2009)
Temperate deciduous forest	Alfisol, 0–5 cm	2.0	4.7	75	288–369	1.5–104	Crow et al. (2007)
Temperate coniferous forest	Inceptisol, 0–5 cm	2.0	4.9	57	73–115	70–149	Crow et al. (2007)
Temperate coniferous forest	Spodosol, EA horizon	2.0	n.a. ^d	20	260–590	6–710	Schulze et al. (2009)
Temperate coniferous forest	Spodosol, Bsh horizon	2.0	n.a.	45	390–460	220–540	Schulze et al. (2009)
Temperate coniferous forest	Spodosol, Bv horizon	2.0	n.a.	70	1420–2170	280–1880	Schulze et al. (2009)
Temperate grassland	Sandstone-derived soil, 0–15 cm	2.0	0.89	78	35.6–65.8	8.6–10.2	Torn et al. (2013)
Temperate grassland	Sandstone-derived soil, 15–30 cm	2.0	0.64	88	32.2–139	8.9–13.7	Torn et al. (2013)
Temperate grassland	Serpentine-derived soil, 0–15 cm	1.8	1.41	72	89.5–133	20–20.3	Torn et al. (2013)
Temperate agricultural ecosystem	Alfisol, 0–25 cm	2.0	5.9	62	108–1050	150–225	Sollins et al. (2009)

^a Density cutoffs for the separation of a light fraction (free or occluded organic C) and a dense fraction (mineral-associated organic C) from bulk soil ([Golchin et al., 1994](#); [Kleber et al., 2014](#)).

^b Mineral-organic associations.

^c Soil organic carbon.

^d “n.a.” in Table 1 means “not available”.

([Kleber et al., 2014](#)).

An important process of mineral-organic association formation and stabilization is the adsorption of SOC to the surfaces of metal oxides ([Omoike and Chorover, 2004](#); [Cagnasso et al., 2010](#)) and phyllosilicates

([Cuba-Chiem et al., 2008](#); [Borer and Hug, 2014](#)). Hydroxamate and carboxyl groups of organic carbon compounds may participate in ligand-exchange reactions with hydroxyls of metal oxide surfaces ([Boily et al., 2000](#); [Borer and Hug, 2014](#)). Organic ligands such as

carboxymethyl cellulose may be adsorbed by non-charged siloxane surfaces of kaolin-group minerals and talc-pyrophyllite (Cuba-Chiem et al., 2008; Kleber et al., 2014), and variable-charge surfaces of phyllosilicates (von Lützow et al., 2006; Liu et al., 2008), which may be influenced by biogeochemical Si cycle (Lucas, 2001; Song et al., 2014).

Organic ligand co-precipitation by Fe and Al is another mechanism of mineral-organic association formation and stabilization (Masion et al., 2000). Fe and Al organic co-precipitates are formed through several interacting processes including complexation of SOC with hydrolyzed species of Fe and Al, precipitation of metal-organic complexes, and adsorption of SOC to the surface of Fe and Al oxides (Masion et al., 2000; Mikutta et al., 2007, 2009). Controlled by the initial metal C ratio, co-precipitates may bind more SOC than adsorption complexes (Kleber et al., 2014).

Contrary to SOC stabilization, some natural or anthropogenic changes of soil conditions may destabilize mineral-organic associations and result in soil disaggregation, which decreases SOC stability (Kleber et al., 2011; Torn et al., 2013; Keiluweit et al., 2015). Mineral-organic associations may be destabilized through many processes including desorption (Feng et al., 2014), surface displacement as a result of competitive sorption (Scott and Rothstein, 2014), and mineral dissolution and transformation (Henderson et al., 2012). The relative importance of the mechanisms depends not only on the properties of mineral-organic associations (Kleber et al., 2014), but also on the time scale, and for deep soil carbon on the priming effect (Fontaine et al., 2007; Hatté et al., 2017). Mineral dissolution and transformation in the vicinity of roots play a more significant role in the long-term destabilization of mineral-organic associations than other mechanisms (Augusto et al., 2001; Turpault et al., 2007; Collignon et al., 2012).

4. Interactions between Si cycle and SOC stability

The biogeochemical C cycle is coupled with cycles of Si and other mineral elements in terrestrial ecosystems through complex interactions (Street-Perrott and Barker, 2008; Song et al., 2012a; Doetterl et al., 2015). The terrestrial biogeochemical Si cycle may influence SOC stability either directly through the protection of SOC by amorphous Si (Toma et al., 2013; Parr and Sullivan, 2014; Zhang et al., 2016), or indirectly through controlling the stabilization and destabilization processes of mineral-organic associations and soil aggregates (Zunino et al., 1982; Pokrovski et al., 2003; Matus et al., 2014). These will be discussed in the following sections.

4.1. SOC stability directly affected by Si

Based on vertical distribution in soils, turnover time estimation and direct dating, amorphous Si forms such as phytoliths are more stable than SOC under most natural soil conditions (Parr and Sullivan, 2005; Song et al., 2016; Zuo et al., 2016, 2017). Contents of phytoliths and SOC in most soil profiles decrease with depth and are comparatively low (Fig. 3a, b) (Alexandre et al., 1997, 2011; Jobbágy and Jackson, 2000; Blecker et al., 2006). Although the relation between soil phytolith and SOC may vary between ecosystems (Alexandre et al., 1997, 2011; Zhang et al., 2016), similarities in the decreasing trends of biogenic Si and SOC with depth for most soil profiles (Fig. 3a, b) plus significant positive correlations between biogenic Si and SOC (Fig. 4a, b) demonstrate that the distribution and stability of SOC are closely related to the turnover of amorphous Si though no cause-effect relationships can be demonstrated currently.

Biogenic Si in most soils consists mainly of phytoliths, which are released from the decomposition of plants (Parr and Sullivan, 2005). Although there is no evidence of a direct chemical interaction between Si and C in plants, Watteau and Villemin (2001) found that some phytoliths closely related with hemicellulose, cellulose and pectic substances were formed in the leaf and root cell walls of beech, whereas pure silica as a layer remained in close proximity with

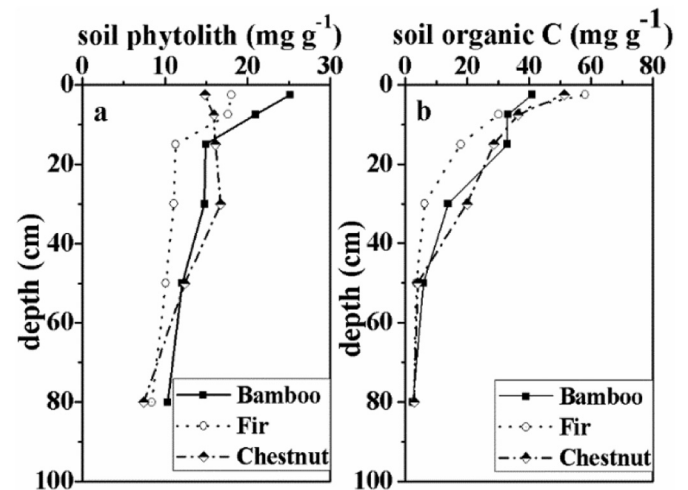


Fig. 3. Vertical distribution of (a) phytoliths and (b) soil organic carbon (C) with depth in soil profiles of three forests (based on Table 1 of Zhang et al., 2016).

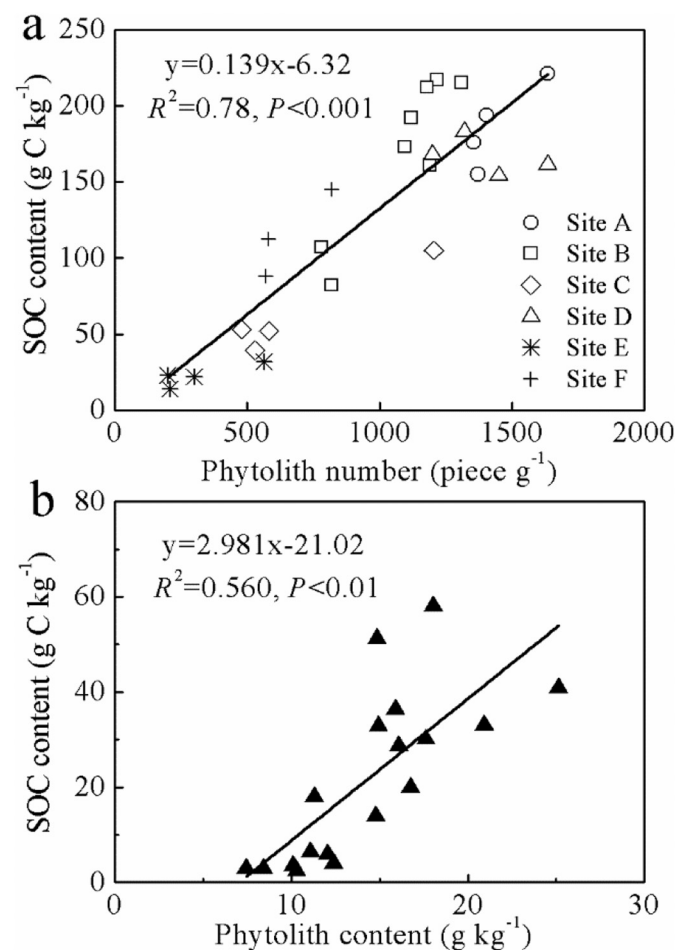


Fig. 4. Relation between soil phytolith and soil organic carbon (SOC). a) Correlation between total number of phytolith and SOC content in soils under grassland (Toma et al., 2013); b) Correlation between phytolith and SOC contents in soils under subtropical forest (Based on Table 1 of Zhang et al., 2016).

polyphenolic substances in the cortical cells of beech roots. During the formation of plant phytoliths, 0.1–5.8% of the organic C may be occluded within silica structure for most plants (Parr and Sullivan, 2005; Yin et al., 2014; Alexandre et al., 2015, 2016). This will mainly be

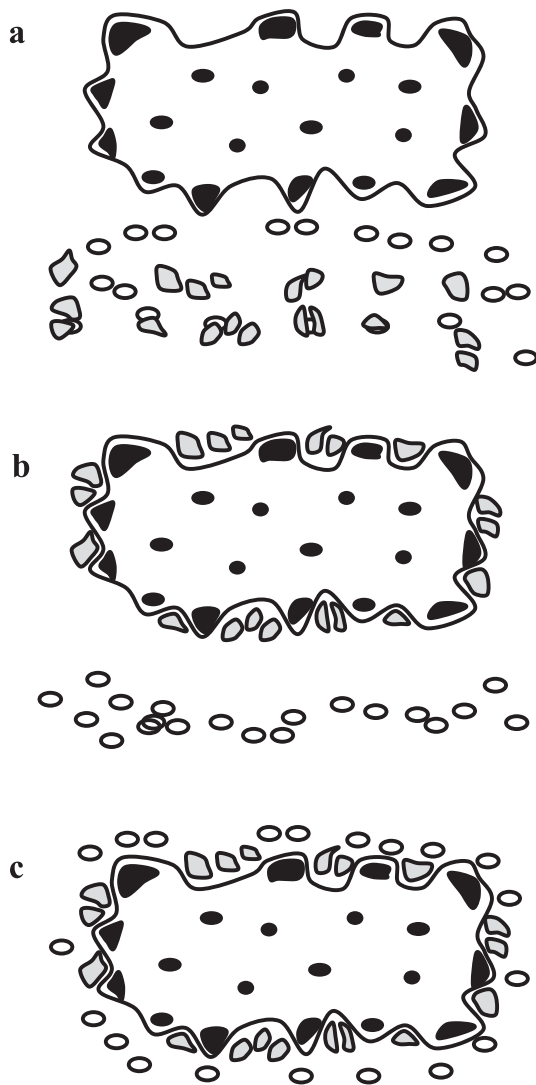


Fig. 5. Visualization of soil organic carbon (SOC) protection by biogenic silicon (Si) (e.g., phytolith, diatom, microbial and protozoic Si) with multiporous structure and large specific area (based on Parr and Sullivan, 2014; Song et al., 2016). a) Input of fresh biogenic Si into the soil. b) Filling or close adsorption of SOC in the cavities of biogenic Si at the early stage of soil biogenic Si accumulation. c) Loose adsorption of SOC on the surface of biogenic Si at the late stage of soil biogenic Si accumulation. Filled black blocks represent organic matter occluded within biogenic Si. Filled gray blocks represent SOC filled or closely adsorbed in the cavities of biogenic Si. Open blocks represent SOC loosely adsorbed on the surface of biogenic Si.

derived from plant photosynthesis as confirmed by recent dating results of phytolith-occluded C, which were very close to those dated with other C materials (Piperno, 2016; Zuo et al., 2016, 2017); however, it has to be noted that there is still some dispute on the possibility of old SOC contribution to the phytolith-occluded C pool (Alexandre et al., 2016; Piperno, 2016; Zuo et al., 2016, 2017). Organic C occluded by phytoliths can be stable in soils for hundreds or thousands of years (Wilding, 1967; Piperno, 2016; Zuo et al., 2016, 2017). The importance of phytolith C sequestration in terrestrial ecosystems has recently been investigated (Parr and Sullivan, 2005; Song et al., 2013, 2016) and will not be discussed in detail in this review. Furthermore, although Watteau and Vilemin (2001) reported the presence of soil silica-organic material and its implication in C stabilization was suspected (Eusterhues et al., 2005a, 2005b), its structure and contribution to SOC stability remain to be investigated.

Similar to the formation and stabilization processes of mineral-

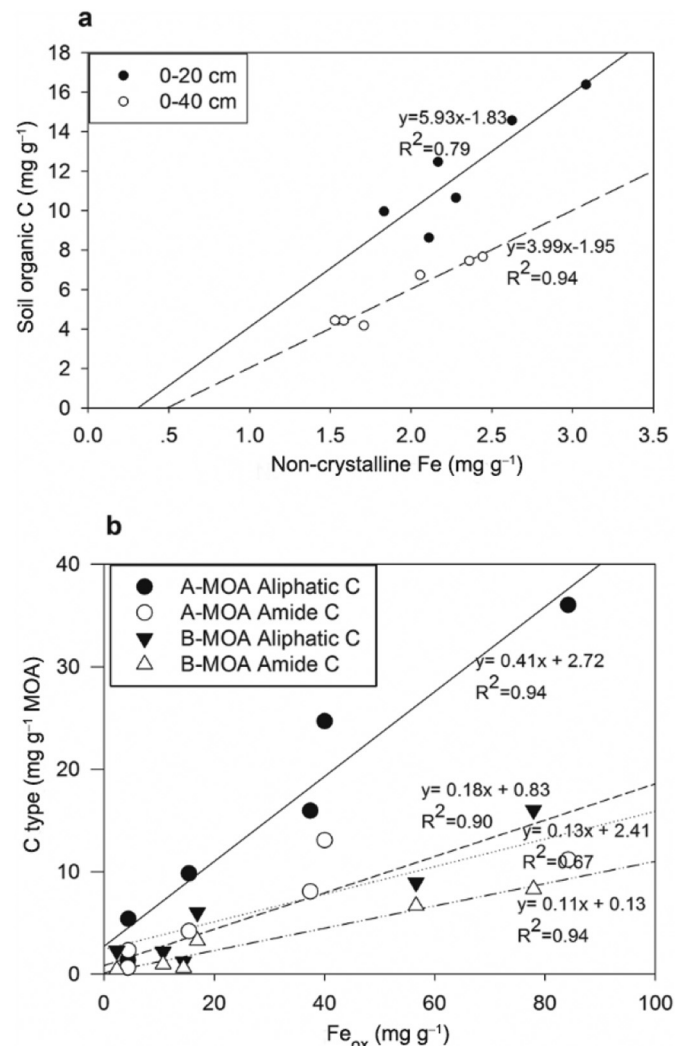


Fig. 6. Relationship between soil organic carbon (SOC) and iron (Fe) (based on data of Mikutta et al., 2009; Zhang et al., 2013): a) Correlation of SOC and non-crystalline Fe in two horizons of ferrallosols after long-term application of organic manure and inorganic fertilizers. b) Correlation of SOC and oxalate-extractable Fe in mineral-organic associations (MOA) from A and B horizons across a soil age gradient (0.3–4100 10^3 year). Oxalate-extractable Fe concentration represents the average of bulked mineral-organic associations. Aliphatic- and Amide- C represent the average composition of SOC located at the surface of these mineral-organic associations.

organic associations (Cuba-Chiem et al., 2008; Borer and Hug, 2014), the stabilization of SOC by amorphous Si in soils is mainly controlled by two processes, the filling of cavities (usually $< 2 \mu\text{m}$ in diameter) of biogenic Si by SOC and the adsorption of SOC to surfaces of amorphous Si (Fig. 5).

Some SOC can be filled in or closely adsorbed to the cavities of biogenic Si at the early stage of biogenic Si accumulation in soil profiles. Biogenic Si is formed mainly in the cell walls, which contain many cavities. However, even apparently solid biogenic Si has been demonstrated to contain cavities (usually $< 0.5 \mu\text{m}$ in diameter) (Carter, 2009; Parr and Sullivan, 2014).

Other SOC can be loosely adsorbed on the surfaces of biogenic Si and other amorphous Si in soil profiles. Both biogenic and lithogenic amorphous Si usually have high specific areas ranging from $5 \text{ m}^2 \text{ g}^{-1}$ to $316 \text{ m}^2 \text{ g}^{-1}$ providing ample sorptive protection sites (Frayse et al., 2009; Loucaides et al., 2010; Diedrich et al., 2012). Partial dissolution of amorphous Si may further increase the pitting degree and specific area of amorphous Si (Frayse et al., 2009), and thus increase the

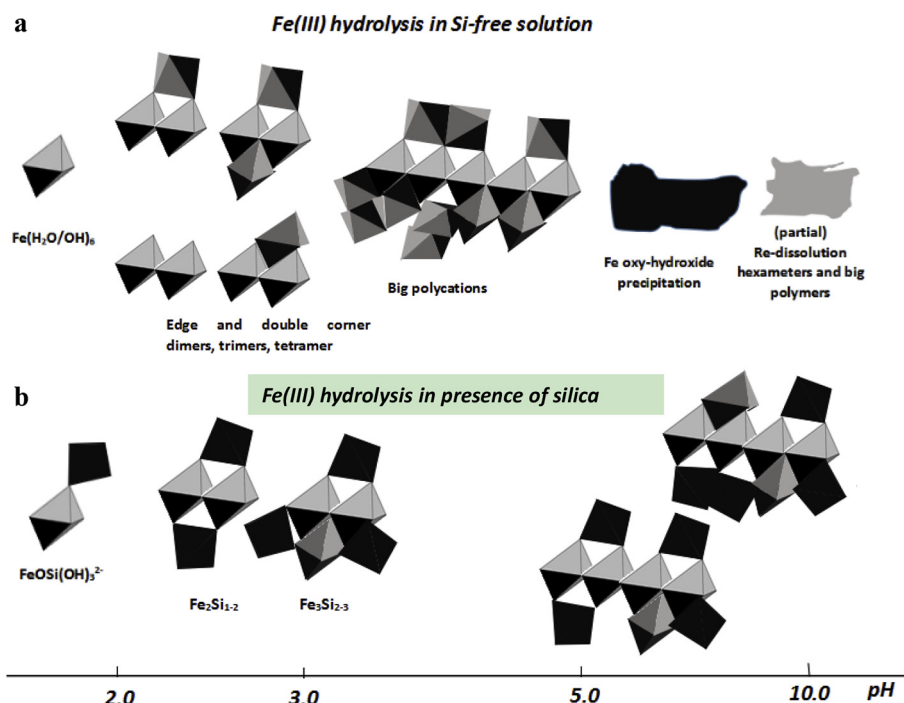


Fig. 7. Variations of Fe(III) hydrolysis in (a) Si-free solution and (b) moderately concentrated Si-solution at different pH values (redrawn from Pokrovski et al., 2003). Octahedra represents the first atomic shell of $\text{Fe}(\text{O}/\text{OH}/\text{H}_2\text{O})_6$ while tetrahedra represents the silicate moieties of $\text{Si}(\text{O}/\text{OH})_4$ for polymers or monomeric silicic acid.

potential for SOC stabilization.

As the storage of biogenic and lithogenic amorphous Si in most soil profiles is high ($1.0 \times 10^4 \text{ kg ha}^{-1}$ to $1.7 \times 10^5 \text{ kg ha}^{-1}$) (Fig. 1, Alexandre et al., 1997; Meunier et al., 1999), the dynamics of soil amorphous Si may significantly influence SOC stability.

4.2. SOC stability regulated by interactions between Si and Fe

Silicon may indirectly regulate SOC stability through influencing the biogeochemical transfer and transformation of Fe (Hiemstra et al., 2007; Jones et al., 2009; Gauger et al., 2016) because SOC stability may be significantly influenced by biogeochemical behavior of Fe (Wagai and Mayer, 2007; Adhikari et al., 2016; Zhao et al., 2016).

Iron may influence the turnover of SOC as reactive Fe oxides may reach up to 180 mg g^{-1} in soils (Wagai and Mayer, 2007; Wagai et al., 2013) and have much higher sorption coefficients for aromatic and lignin-derived organic carbon than other metal oxides (Kaiser et al., 1997; Chorover and Amistadi, 2001; Mikutta et al., 2007). Fe-bound SOC content in soils may reach 22 mg g^{-1} soil, approximately 40% of SOC for forest soils (Wagai and Mayer, 2007; Zhao et al., 2016). Significantly positive correlations of aliphatic and amide C with oxalate-extractable Fe concentrations (Fig. 6) in moist soils further demonstrate that poorly crystalline Fe phases such as ferrihydrite/nanocrystalline goethite may also preferentially associate with microbial C (Lehmann et al., 2008; Mikutta et al., 2009). Understanding the fate of Fe(III) oxides is essential to evaluate the turnover and stability of Fe-bound SOC.

Ferric minerals in some soil environments may undergo redox reactions, which may destroy Fe(III) oxide-SOC complexes and destabilize Fe-bound OC (Adhikari et al., 2016; Pan et al., 2016). Adhikari et al. (2016) recently investigated the release processes of Fe and Fe-bound OC during the reduction of hematite-humic acid complexes by dithionite. They found that the Fe-bound OC was readily released with a release rate constant of $0.011\text{--}1.49 \text{ min}^{-1}$ during the initial stage, a rate much higher than that of Fe with a release rate constant of $6.67\text{--}13.0 \times 10^{-3} \text{ min}^{-1}$. However, Zhao et al. (2017) reported that the fraction of Fe-bound OC released was positively correlated with the

fraction of Fe reduced over an 8-day anaerobic reduction period with Fe-reducing bacterium, *Shewanella oneidensis* MR-1. Therefore, it is important to investigate the behavior of Fe in soil profiles to more accurately estimate the turnover and stability of Fe-bound SOC.

Dissolved Si released from the dissolution of biogenic and lithogenic amorphous Si, and silicate weathering (Fig. 1) may enhance Fe(II) oxidation rate (Gauger et al., 2016). Dissolved Si may also interact with Fe(III) through many processes such as inhibition of Fe(III) hydrolysis and polymerization, and reduction of the transformation of poorly crystalline minerals to more stable crystalline Fe(III) phases (Pokrovski et al., 2003; Hiemstra et al., 2007; Jones et al., 2009), and thus influence the distribution of poorly crystalline Fe phases and SOC stability in soil profiles.

Dissolved Si may significantly inhibit the hydrolysis, polymerization and solid-phase growth of Fe (III) in solution through forming iron silicate aqueous complexes (Konhauser and Ferris, 1996; Pokrovski et al., 2003), and thus increasing the mobility of Fe (III). For example, using X-ray absorption fine structure spectroscopy at the Fe K-edge, Pokrovski et al. (2003) found that Fe is hexacoordinated with 6 oxygens of H_2O - and/or OH-groups at pH lower than 2.5, bridged with hydroxyls ($-\text{OH}-$) or oxygens ($-\text{O}-$), and polymerized by $\text{Fe}(\text{O}/\text{OH})\text{-Fe}$ bonds at pH ranging between 2.5 and 13 in Si-free solutions (Fig. 7a), whereas Fe may complex with Si to form $\text{Fe}_2\text{Si}_{1-2}$ and $\text{Fe}_3\text{Si}_{2-3}$ at pH smaller than 3 in a $0.05\text{-}m$ Si solutions and partially substitute Si in the tetrahedral silica polymers in solutions at higher Si concentration (Fig. 7b). The increased mobility of Fe (III) from such complexation of dissolved Si in soil profiles may result in deeper distribution of poorly crystalline Fe phases and their stably protected SOC.

Dissolved Si may also reduce the Fe(II)-catalyzed transformation of poorly crystalline minerals such as ferrihydrite to more stable crystalline Fe(III) phases such as goethite mainly through two mechanisms (Pedersen et al., 2005; Jones et al., 2009). In the first mechanism, dissolved Si reduces the adsorption of aqueous Fe(II) through competitive adsorption, and thus inhibits electron/isotope exchange between mineral Fe(III) and aqueous Fe(II) (Jones et al., 2009). The second mechanism is that dissolved Si prevents the polymerization and recrystallization of Fe(III) into a more stable, crystalline Fe(III) mineral

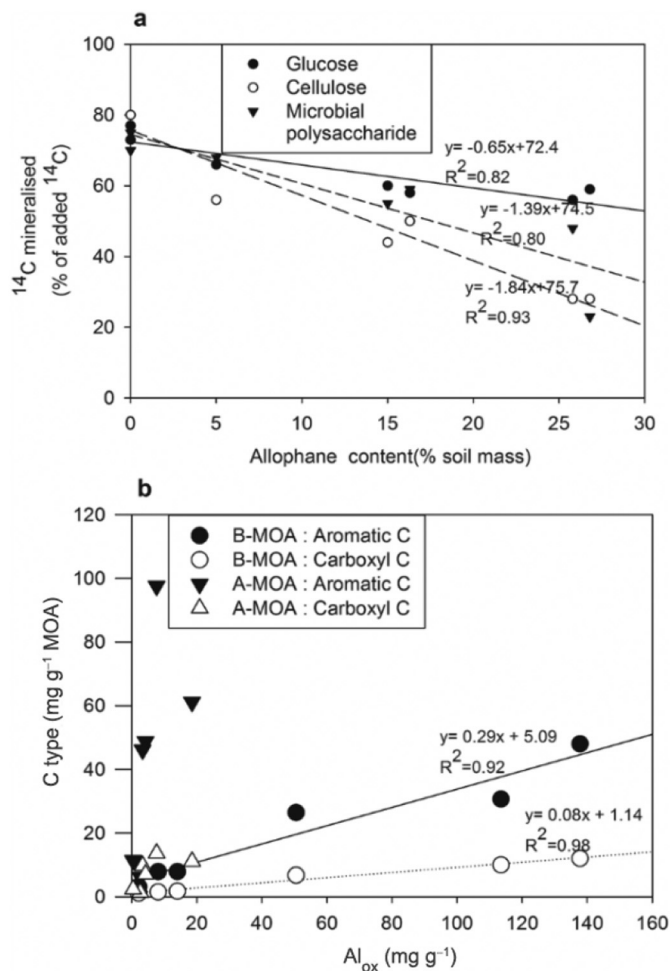


Fig. 8. Relationship between soil organic carbon (SOC) and aluminum (Al) in soils (after Zunino et al., 1982; Mikutta et al., 2009): a) Impact of the soil's allophane content on the mineralization of ^{14}C -labeled organic C fractions including glucose, cellulose, and microbial polysaccharide in a laboratory incubation study. b) Correlation of aromatic and carboxy C with oxalate-extractable Al (Al_{ox}).

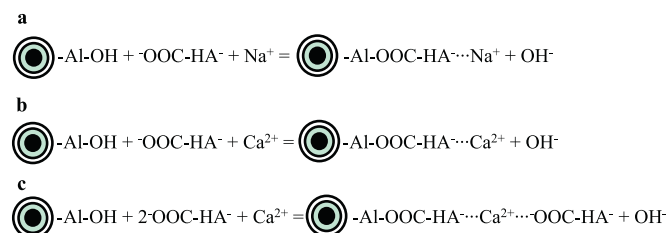


Fig. 9. Ligand exchange mechanisms of soil allophane (model $\text{Al}_2\text{Si}_2\text{O}_5\text{nH}_2\text{O}$) and humic acids with carboxylate groups ($\text{HA} + \text{carboxylate}$) (modified from Yuan et al., 2000; Matus et al., 2014): a) in NaCl; in CaCl_2 with concentrations of humic acids b) < 25 and c) $> 25 \text{ mg L}^{-1}$ organic C.

(Pedersen et al., 2005; Jones et al., 2009). As the C stabilization capacity of Fe phases generally decreases with the crystalline degree (Mikutta et al., 2009), dissolved Si-inhibited Fe(III) crystallization may substantially increase SOC stability. However, the rates and the time scales involved in dissolved Si-inhibited Fe(III) crystallization processes and their effects on SOC stability need to be investigated in detail.

4.3. SOC stability regulated by interactions between Si and Al

Similar to the regulation of SOC stability through Si-Fe interactions

discussed above, Si may also indirectly regulate SOC stability via affecting the biogeochemical Al cycle in soil-plant systems (Hodson and Sangster, 1999; Lucas, 2001; Barré et al., 2009). The stability of SOC may be significantly influenced by different forms of Al such as Al-humus complexes and allophane/imogolite (Mizota and van Reeuwijk, 1989; Buurman et al., 2007; Takahashi and Dahlgren, 2016).

Al-humus complexes may protect SOC directly by rendering condensed functional groups less accessible to biological and enzymatic attack (Rasmussen et al., 2006) and indirectly by promoting the formation of Al-humic-mineral complexes and cementation of soil particles (Oades, 1988). However, the complexation of Al^{3+} by humic substances may be less important for SOC stabilization than other processes such as aluminum silicate clay mineral stabilization (Buurman et al., 2007). An exception is Andosols because of their distinctive properties including variable charge, high water retention and low bulk density (Shoji et al., 1993). Aluminum in Andosols under humid climatic conditions usually forms a continuum between Al-humus complexes and allophane/imogolite (Mizota and van Reeuwijk, 1989; Takahashi and Dahlgren, 2016). Both the formation of Al-humus complexes and allophane/imogolite may effectively stabilize SOC against decomposition (Takahashi and Dahlgren, 2016).

SOC can also be stabilized by Si-Al secondary clay minerals (e.g., allophane and kaolinite) and their nano-, micro- and macro-aggregates (Boudot et al., 1988; Baldock and Skjemstad, 2000; Matus et al., 2014; Huang et al., 2016). For example, Zunino et al. (1982) found that the mineralization of ^{14}C -labeled organic C fractions decreased almost linearly with a soil's allophane content (Fig. 8) implying the significant control of allophane on the biological stabilization of SOC. This may be controlled by a ligand exchange mechanism of allophane (model $\text{Al}_2\text{Si}_2\text{O}_5\text{nH}_2\text{O}$) and SOC with carboxylate groups ($\text{HA} + \text{carboxylate}$) (Fig. 9) because allophane usually has a large specific surface area of about $800 \text{ m}^2 \text{ g}^{-1}$ (Matus et al., 2014). The stabilization of SOC by Si-Al secondary clay minerals depends not only on the chemical structure and morphology of SOC but also on the type, physico-chemical properties and distribution of the clay minerals (Baldock and Skjemstad, 2000).

The interactions between Si and Al may occur both in plant tissues during the precipitation of phytoliths (Bartoli and Wilding, 1980; Hodson and Sangster, 1999) and in soil profiles during the transport of Si and Al dissolved in soil solutions and subsequently precipitated as secondary minerals (Lucas, 2001).

The distribution of Al and Si in plant tissues varied with species, but Al was invariably co-precipitated with Si through forming Al-Si complexes (Hodson and Sangster, 1999; Britz et al., 2002; Lima et al., 2016). However, the Al/Si ratio of the deposits varies greatly among species. For example, detailed chemical examination of phytoliths from pine and beech indicates that Al/Si ratio of bulk phytoliths in pine (8.5) is much lower than that in beech (18.9) (Bartoli, 1985). The Al-Si deposits released from the decomposition of annual plant litter may partly accumulate in soils and/or sediments (Wüst and Bustin, 2003; Parr and Sullivan, 2005).

Although soil secondary clay minerals such as kaolinite and allophane have traditionally been considered as the weathering products of primary silicate minerals (Matus et al., 2014), increasing evidence suggests that plants may control the terrestrial biogeochemical Si cycle (Fig. 1), influence the distribution of dissolved Al or aluminum oxides through forming Al-Si complexes, and thus alter the types, physico-chemical properties and vertical distribution of Si-Al clay minerals (Jobbágy and Jackson, 2001; Lucas, 2001; Barré et al., 2009) and/or hydroxyaluminosilicates (Doucet et al., 2001) in soil profiles. For example, kaolinitic topsoil horizons (3- to 8-m-thick) were developed on gibbsitic horizons (approximately 3-m-thick) in most humid tropic soils mainly due to intense biological activities and biogeochemical cycles of elements, especially Si and Al (Lucas et al., 1993).

Anthropogenic activities such as silicate application, changes in land use and land cover, and biomass harvest may significantly affect the biogeochemical Si cycle in terrestrial ecosystems and the

Table 2

Measures to enhance soil C sequestration through manipulating the Si cycle based on feedback mechanisms between Si, Fe, Al and C (Lal, 2004a, 2004b; Song et al., 2012b, 2014; Huang et al., 2014).

Mechanism	Measure types	Measures	High potential in ecosystem types
Biogenic Si protection	Soil amendment	Organic mulching	Croplands and bamboo ecosystems
		Silicate rock powder amendment	Croplands and bamboo ecosystems
	Plant regulation	Silicon and biochar fertilization	Acidic soils
		Cultivation of Si-rich plants	Croplands and bamboo ecosystems
Interactions between Si-Fe and Si-Al	Soil amendment	Grazing and fire management	Grasslands
		Genetic engineering of plants	Croplands
		Organic mulching	Croplands and bamboo ecosystems
		Organic manure application	Croplands on acidic soils such as ferrasols
	Plant regulation	Basalt powder amendment	Croplands and bamboo ecosystems
		Silicon and biochar fertilization	Acidic soils
		Cultivation of Si-rich plants	Croplands and bamboo ecosystems

distribution and stability of Si-Al secondary clay minerals, and thus SOC stability (Wiesmeier et al., 2012; Whitmore et al., 2015).

5. Manipulating the Si cycle to enhance soil C sequestration

The “4 per mille Soils for Food Security and Climate” was recently proposed to increase global SOC stocks by 4 per 1000 (i.e., 0.4%) per year and mitigate the anthropogenic emissions of greenhouse gases globally. However, the SOC sequestration potential varies with region specific initial SOC stocks and management practices of soil C sequestration (Minasny et al., 2017). As the terrestrial biogeochemical Si cycle may influence SOC stability either directly or indirectly (Fig. 5-9), management practices that regulate the biogeochemical Si cycle in soil profiles such as soil amendments, plant regulations including cultivation of Si-rich plants and grazing management can be used to enhance soil C sequestration in terrestrial ecosystems. These practices to enhance soil C sequestration can be classified according to the controlling mechanisms into measures of biogenic Si protection, Si-Fe and Si-Al interactions (Table 2).

Measures to enhance soil C sequestration through biogenic Si protection include organic mulching, silicate rock powder amendment, silicon and biochar fertilization, cultivation of Si-rich plant, and genetic engineering of plants (Table 2). For example, the amendment of Si-containing materials such as organic mulch (Huang et al., 2014), silicate rock powder (Guo et al., 2015) and slag-based silicate fertilizer (Song et al., 2015) may significantly enhance the supply of bioavailable Si, increase the plant production and soil accumulation of phytoliths, and thus increase SOC stability through phytolith C sequestration and biogenic Si protection (Fig. 5). However, the C sequestration effects and costs of different management practices differ among ecosystems (Table 2). For croplands and intensively managed bamboo ecosystems, organic mulching and cultivation of Si-rich plant species are more efficient in C sequestration than other measures. In contrast, for grasslands, grazing and fire management are currently more suitable than other measures due to their relatively low costs and wide distribution of grasslands.

Measures to enhance soil C sequestration through interactions of Si-Fe and Si-Al include organic mulching, silicate rock powder amendment, Si and biochar fertilization and cultivation of Si-rich plants (Table 2). For example, the cultivation of Si-accumulating plants such as bamboo may accelerate silicate weathering, enhance the accumulation of secondary minerals (Song et al., 2011), and thus also SOC stability through Si-Fe and Si-Al interactions.

Similar to traditional C input practices such as organic mulching and organic manure application, many studies revealed that Si fertilization increased plant growth under various abiotic (Liang et al., 2005; Pei et al., 2010; Cooke and Leishman, 2016) and biotic (Reynolds et al., 2009; Van Bockhaven et al., 2015; Hartley and DeGabriel, 2016) stresses, which could lead to higher C input into soils and accelerate SOC accumulation.

The above measures for enhancing soil C sequestration through regulating the biogeochemical Si cycle in terrestrial ecosystems are promising as soil Si amendments may also enhance plant use efficiency of some nutrients such as nitrogen, phosphorus and potassium under low supply conditions (Marxen et al., 2016; Kostic et al., 2017) and inhibit plant nutrient use under excessive supply conditions (Ma and Takahashi, 1990; Broadley et al., 2012; Hu et al., 2017). However, the effects of different soil Si amendments on plant nutrient use efficiency under various nutrient supply conditions should be compared. Furthermore, more detailed quantification of efficiency, costs and potential combinations of such measures to enhance soil C sequestration through biogenic Si protection are required before their wide application.

6. Conclusions

The terrestrial biogeochemical Si cycle may significantly influence the processes of SOC stabilization either directly through the protection of SOC by amorphous Si, or indirectly through controlling the dynamics of Al and Fe secondary phases, stabilization and destabilization processes of mineral–organic associations and soil aggregates, and thus plays an important role in the global C cycle and climate change. The strategic manipulation of the Si cycle in terrestrial ecosystems offers a new opportunity to enhance soil C sequestration. Rock powder amendment, establishment of Si-rich plant buffer strips and innovative management practices that return Si-rich biomass materials to soil can be implemented as strategies to enhance soil C sequestration through regulating terrestrial Si cycle. However, research in the following areas is required to fully understand and quantify the effects of the terrestrial biogeochemical Si cycle on SOC stabilization:

- (1) Investigating the distribution and biogeochemical cycle of Si in soils developed on different parent materials and under different climatic and vegetation conditions together with SOC distribution and stabilization with promising approaches such as electron microscopy with energy dispersive (X-ray SEM-EDX), transmission electron microscope (TEM), nano secondary ion mass spectrometer (NanoSIMS) can effectively untangle the mechanisms responsible for the role of Si in the SOC stability.
- (2) The relative contribution of chemical weathering of silicate minerals and input of phytogenic, protozoic and microbial Si to the soil dissolved Si and secondary Si minerals in soil profiles from different terrestrial ecosystems should be quantified.
- (3) The interaction mechanisms of Si, Fe and Al should be investigated under both controlled experiments and field investigations. More importantly, the surface properties (e.g., specific surface area and adsorption potential of SOC) of biogenic Si and mineral–organic associations need to be analyzed in detail.
- (4) The relative importance of amorphous Si protection, Si-Fe interactions and Si-Al interactions in controlling SOC stabilization for different terrestrial ecosystems has not been quantified yet. Field

- experiments are needed to examine the effects of potential measures on the terrestrial Si cycle and SOC stabilization.
- (5) More comparing experiments of Si amendment under different environmental conditions (e.g., arid and submerged conditions) and different experimental treatments (e.g., different Si sources and doses) are required to improve the understanding of the role of Si in straw/litter decomposition and soil respiration.
 - (6) How to quantify and balance the potential and cost of each measure to enhance soil C sequestration? How to better combine different measures to more efficiently enhance soil C sequestration? Solving these questions may guide the manipulation of soil C sequestration in terrestrial ecosystems.
 - (7) Global C cycle models should incorporate the mechanism of SOC stabilization coupled with the biogeochemical Si cycle in terrestrial ecosystems to improve our understanding on the effects of management practices on global C balance and climate change.

Conflict of interest

The authors declare no conflict of interest.

Acknowledgments

The research was supported by National Natural Science Foundation of China (41522207 and 41571130042) and the State's key Project of Research and Development Plan of China (2016YFA0601002 and 2017YFC0212703).

References

- Adhikari, D., Poulson, S.R., Sumaila, S., Dynes, J.J., McBeth, J.M., Yang, Y., 2016. Asynchronous reductive release of iron and organic carbon from hematite–humic acid complexes. *Chem. Geol.* 430, 13–20.
- Alexandre, A., Meunier, J.D., Colin, F., Koud, J.M., 1997. Plant impact on the biogeochemical cycle of silicon and related weathering processes. *Geochim. Cosmochim. Acta* 61, 677–682.
- Alexandre, A., Bouvet, M., Abbadie, L., 2011. The role of savannas in the terrestrial Si cycle: a case-study from Lamto, Ivory Coast. *Glob. Planet. Chang.* 78, 162–169.
- Alexandre, A., Basile-Doelsch, I., Delhay, T., Borshneck, D., Mazur, J.C., Reyerson, P., Santos, G.M., 2015. New highlights of phytolith structure and occluded carbon location: 3-D X-ray microscopy and NanoSIMS results. *Biogeosciences* 12, 863–873.
- Alexandre, A., Balesdent, J., Cazeville, P., Chevassus-Rosset, C., Signoret, P., Mazur, J.C., Harutyunyan, A., Doelsch, E., Basile-Doelsch, I., Mische, H., Santos, G.M., 2016. Direct uptake of organically derived carbon by grass roots and allocation in leaves and phytoliths: ^{13}C labeling evidence. *Biogeosciences* 13, 1693–1703.
- Ali, M.A., Lee, C.H., Kim, P.J., 2008. Effect of silicate fertilizer on reducing methane emission during rice cultivation. *Biol. Fert. Soils* 44, 597–604.
- Aoki, Y., Hoshino, M., Matsubara, T., 2007. Silica and testate amoebae in a soil under pine-oak forest. *Geoderma* 142, 29–35.
- Augusto, L., Ranger, J., Turpault, M.P., Bonnaud, P., 2001. Experimental in situ transformation of vermiculites to study the weathering impact of tree species on the soil. *Eur. J. Soil Sci.* 52, 81–92.
- Austin, A.T., Méndez, M.S., Ballaré, C.L., 2016. Photodegradation alleviates the lignin bottleneck for carbon turnover in terrestrial ecosystems. *P. Natl. Acad. Sci.* 113, 4392–4397.
- Baillieu, B., Berne, N., Murik, O., Petroustos, D., Prihoda, J., Tanaka, A., Villanova, V., Bligny, R., Flori, S., Krieger-Liszka, A., Santabarbara, S., Rappaport, F., Joliet, P., Tirichine, L., Falkowski, P.G., Cardol, P., Bowler, C., Finazzi, G., 2015. Energetic coupling between plastids and mitochondria drives CO_2 assimilation in diatoms. *Nature* 524, 366–369.
- Baldock, J.A., Skjemstad, J.O., 2000. Role of the soil matrix and minerals in protecting natural organic materials against biological attack. *Org. Geochem.* 31, 697–710.
- Barré, P., Berger, G., Velde, B., 2009. How element translocation by plants may stabilize illitic clays in the surface of temperate soils. *Geoderma* 151, 22–30.
- Bartoli, F., 1985. Crystallochemistry and surface properties of biogenic opal. *Eur. J. Soil Sci.* 36, 335–350.
- Bartoli, F., Wilding, L.P., 1980. Dissolution of biogenic opal as a function of its physical and chemical properties. *Soil Sci. Soc. Am. J.* 44, 873–878.
- Basile-Doelsch, I., Meunier, J.-D., Parron, C., 2005. Another continental pool in the terrestrial silicon cycle. *Nature* 433, 399–402.
- Berner, R.A., 1997. The rise of plants and their effect on weathering and atmospheric CO_2 . *Science* 276, 544–546.
- Blecker, S.W., McCulley, R.L., Chadwick, O.A., Kelly, E.F., 2006. Biologic cycling of silica across a grassland bioclimosequence. *Global Biogeochem. Cy.* 20, 1–11.
- Boily, J.-F., Persson, P., Sjöberg, S., 2000. Benzenecarboxylate surface complexation at the goethite ($\alpha\text{-FeOOH}$)/water interface: II. Linking IR spectroscopic observations to mechanistic surface complexation models for phthalate, trimellitate, and pyromellitate. *Geochim. Cosmochim. Acta* 64, 3453–3470.
- Borer, P., Hug, S.J., 2014. Photo-redox reactions of dicarboxylates and α -hydroxydicarboxylates at the surface of Fe(III) (hydr)oxides followed with in situ ATR-FTIR spectroscopy. *J. Colloid Interface Sci.* 416, 44–53.
- Boudot, J.P., Bel Hadi Brahim, A., Chone, T., 1988. Dependence of carbon and nitrogen mineralisation rates upon amorphous metallic constituents and allophanes in high-land soils. *Geoderma* 42, 245–260.
- Britez, R.M., Watanabe, T., Jansen, S., Reissmann, C.B., Osaki, M., 2002. The relationship between aluminium and silicon accumulation in leaves of *Faramaea marginata* (Rubiaceae). *New Phytol.* 156, 437–444.
- Broadley, M., Brown, P., Cakmak, I., Ma, J.F., Rengel, Z., Zhao, F.J., 2012. Beneficial elements. In: Marschner, P. (Ed.), *Marschner's mineral nutrition of higher plants*, Third Edition. Science Press, Beijing, pp. 249–269.
- Buurman, P., Peterse, F., Almendros Martin, G., 2007. Soil organic matter chemistry in allophanic soils: a pyrolysis-GC/MS study of a Costa Rican andosol catena. *Eur. J. Soil Sci.* 58, 1330–1347.
- Cagnasso, M., Boero, V., Franchini, M.A., Chorover, J., 2010. ATR-FTIR studies of phospholipid vesicle interactions with $\alpha\text{-FeOOH}$ and $\alpha\text{-Fe}_2\text{O}_3$ surfaces. *Colloids Surf. B* 76, 456–467.
- Campbell, E.E., Paustian, K., 2015. Current developments in soil organic matter modeling and the expansion of model applications: a review. *Environ. Res. Lett.* 10 (12), 123004.
- Carey, J.C., Fulweiler, R.W., 2012. Human activities directly alter watershed dissolved silica fluxes. *Biogeochemistry* 111, 125–138.
- Carter, J.A., 2009. Atmospheric carbon isotope signatures in phytolith-occluded carbon. *Quatern. Int.* 193, 20–29.
- Cermeño, P., Falkowski, P.G., Romero, O.E., Schaller, M.F., Vallina, S.M., 2015. Continental erosion and the Cenozoic rise of marine diatoms. *P. Natl. Acad. Sci.* 112, 4239–4244.
- Chorover, J., Amistadi, M.K., 2001. Reaction of forest floor organic matter at goethite, birnessite and smectite surfaces. *Geochim. Cosmochim. Acta* 65, 95–109.
- Clarke, J., 2003. The occurrence and significance of biogenic opal in the regolith. *Earth-Sci. Rev.* 60, 175–194.
- Clymans, W., Conley, D.J., Battles, J.J., Frings, P.J., Koppers, M.M., Likens, G.E., Johnson, C.E., 2016. Silica uptake and release in live and decaying biomass in a northern hardwood forest. *Ecology* 97, 3044–3057.
- Collignon, C., Ranger, J., Turpault, M.P., 2012. Seasonal dynamics of Al- and Fe-bearing secondary minerals in an acid forest soil: influence of Norway spruce roots (*Picea abies* (L.) Karst.). *Eur. J. Soil Sci.* 63, 592–602.
- Conley, D.J., 2002. Terrestrial ecosystems and the global biogeochemical silica cycle. *Global Biogeochem. Cy.* 16 (68–1–68–8).
- Conley, D.J., Likens, G.E., Buso, D.C., Saccone, L., Bailey, S.W., Johnson, C.S.E., 2008. Deforestation causes increased dissolved silicate losses in the Hubbard brook experimental Forest. *Glob. Chang. Biol.* 14, 2548–2554.
- Cooke, J., Leishman, R.M., 2016. Consistent alleviation of abiotic stress with silicon addition: a meta-analysis. *Funct. Ecol.* 30, 1340–1357.
- Crow, S.E., Swanston, C.W., Lajtha, K., Brooks, J.R., Keirstead, H., 2007. Density fractionation of forest soils: methodological questions and interpretation of incubation results and turnover time in an ecosystem context. *Biogeochemistry* 85, 69–90.
- Cuba-Chiem, L.T., Huynh, L., Ralston, J., Beattie, D.A., 2008. In situ particle film ATR FTIR spectroscopy of carboxymethyl cellulose adsorption on talc: binding mechanism, pH effects, and adsorption kinetics. *Langmuir* 24, 8036–8044.
- Derry, L.A., Kurtz, A.C., Ziegler, K., Chadwick, O.A., 2005. Biological control of terrestrial silica cycling and export fluxes to watersheds. *Nature* 433, 728–731.
- Diedrich, T., Dybowska, A., Schott, J., Valsami-Jones, E., Oelkers, E.H., 2012. The dissolution rates of SiO_2 nanoparticles as a function of particle size. *Environ. Sci. Technol.* 46, 4909–4915.
- Doetterl, S., Stevens, A., Six, J., Merckx, R., Van Oost, K., Pinto, M.C., Casanova-Katny, A., Muñoz, C., Boudin, M., Venegas, E.Z., Boeckx, P., 2015. Soil carbon storage controlled by interactions between geochemistry and climate. *Nat. Geosci.* 8, 780–783.
- Doetterl, S., Berhe, A.A., Nadeu, E., Wang, Z., Sommer, M., Fiener, P., 2016. Erosion, deposition and soil carbon: a review of process-level controls, experimental tools and models to address C cycling in dynamic landscapes. *Earth-Sci. Rev.* 154, 102–122.
- Doucet, F.J., Schneider, C., Bones, S.J., 2001. The formation of hydroxylaluminosilicates of geochemical and biological significance. *Geochim. Cosmochim. Acta* 65, 2461–2467.
- Dove, P.M., 1995. In: White, A.F., Brantley, S.L. (Eds.), *Kinetic and thermodynamic controls on silica reactivity in weathering environments*. Mineralogical Society of America, Washington, DC, pp. 235–290. Chemical weathering rates of silicate minerals.
- Drees, L.R., Wilding, L.P., Smeck, N.E., Sankay, A.L., 1989. Silica in soils: Quartz and disordered silica polymorphs. In: Dixon, J.B., Weed, S.B. (Eds.), *Minerals in Soil Environments*. SSSA Book Series, pp. 913–974 (No. 1, Madison, WI).
- Drever, J.I., Zobrist, J., 1992. Chemical weathering of silicate rocks as a function of elevation in the southern Swiss alps. *Geochim. Cosmochim. Acta* 56, 3209–3216.
- Dunn, R.E., Strömberg, C.A., Madden, R.H., Kohn, M.J., Carlini, A.A., 2015. Linked canopy, climate, and faunal change in the Cenozoic of Patagonia. *Science* 347, 258–261.
- Emmens, W.J., Schoelynck, J., Grootjans, A.P., Struyf, E., van Diggelen, R., 2016. Eutrophication alters Si cycling and litter decomposition in wetlands. *Biogeochemistry* 130, 289–299.
- Epstein, E., 1994. The anomaly of silicon in plant biology. *P. Natl. Acad. Sci.* 91, 11–17.
- Epstein, E., 1999. Silicon. *Ann. Rev. Plant Physiol. Plant Molec. Biol.* 50, 641–664.
- Eusterhues, K., Rumpel, C., Kögel-Knabner, I., 2005a. Organo-mineral associations in sandy acid forest soils: importance of specific surface area, iron oxides and

- micropores. *Eur. J. Soil Sci.* 56, 753–763.
- Eusterhues, K., Rumpel, C., Kögel-Knabner, I., 2005b. Stabilization of soil organic matter isolated via oxidative degradation. *Org. Geochem.* 36, 1567–1575.
- Falkowski, P.G., Scholes, R.J., Boyle, E., Canadell, J., Canfield, D., Elser, J., Gruber, N., Hibbard, K., Höglberg, P., Linder, S., Mackenzie, F.T., Moore, I.L.I., Pedersen, T., Rosenthal, Y., Seitzinger, S., Smetacek, V., Steffen, W., 2000. The global carbon cycle: a test of our knowledge of earth as a system. *Science* 290, 291–296.
- Fauteux, F., Chain, F., Belzile, F., Menzies, J.G., Bélanger, R.R., 2006. The protective role of silicon in the *Arabidophytogenics*–powdery mildew pathosystem. *P. Natl. Acad. Sci.* 103, 17554–17559.
- Feng, W.T., Plante, A.F., Aufdenkampe, A.K., Six, J., 2014. Soil organic matter stability in organo-mineral complexes as a function of increasing C loading. *Soil Biol. Biochem.* 69, 398–405.
- Fontaine, S., Barot, S., Barre, P., Bdioui, N., Mary, B., Rumpel, C., 2007. Stability of organic carbon in deep soil layers controlled by fresh carbon supply. *Nature* 450, 277–280.
- Frayse, F., Pokrovsky, O.S., Schott, J., Meunier, J.-D., 2006. Surface properties, solubility and dissolution kinetics of bamboo phytoliths. *Geochim. Cosmochim. Ac.* 70, 1939–1951.
- Frayse, F., Pokrovsky, O.S., Schott, J., Meunier, J.-D., 2009. Surface chemistry and reactivity of plant phytoliths in aqueous solutions. *Chem. Geol.* 258, 197–206.
- Gao, Y., Yu, G., Yang, T., Jia, Y., He, N., Zhuang, J., 2016. New insight into global blue carbon estimation under human activity in land-sea interaction area: a case study of China. *Earth-Sci. Rev.* 159, 36–46.
- Gauger, T., Byrne, J.M., Konhauser, K.O., Obst, M., Crowe, S., Kappler, A., 2016. Influence of organics and silica on Fe (II) oxidation rates and cell–mineral aggregate formation by the green-sulfur Fe (II)-oxidizing bacterium *Chlorobium ferrooxidans* KoFox–implications for Fe (II) oxidation in ancient oceans. *Earth Planet. Sci. Lett.* 443, 81–89.
- Golchin, A., Oades, J.M., Skjemstad, J.O., Clarke, P., 1994. Study of free and occluded particulate organic matter in soils by solid state ^{13}C CP/MAS NMR spectroscopy and scanning electron microscopy. *Aust. J. Soil Res.* 32, 285–309.
- Guo, F.S., Song, Z.L., Sullivan, L., Wang, H.L., Liu, X.Y., Wang, X.D., Li, Z.M., Zhao, Y.Y., 2015. Enhancing phytolith carbon sequestration in rice ecosystems through basalt powder amendment. *Sci. Bull.* 60, 591–597.
- Hartley, E.S., DeGabriel, L.J., 2016. The ecology of herbivore-induced silicon defences in grasses. *Funct. Ecol.* 30, 1311–1322.
- Hatté, C., Noury, C., Kheirbeik, L., Balesdent, J., 2017. Turnover of the soil organic matter amino acid fraction investigated by ^{13}C and ^{14}C signatures of carboxyl carbon. *Radiocarbon* 59 (2), 473–481.
- Henderson, R., Kabengi, N., Mantripragada, N., Cabrera, M., Hassan, S., Thompson, A., 2012. Anoxia-induced release of colloid- and nanoparticle-bound phosphorus in grassland soils. *Environ. Sci. Technol.* 46, 11727–11734.
- Hiemstra, T., Barnett, M.O., van Riemsdijk, W.H., 2007. Interaction of silicic acid with goethite. *J. Colloid Interface Sci.* 310, 8–17.
- Hinsinger, P., Fernandes Barros, O.N., Benedetti, M.F., Noack, Y., Callot, G., 2001. Plant-induced weathering of a basaltic rock: experimental evidence. *Geochim. Cosmochim. Ac.* 65, 137–152.
- Hodson, M.J., Sangster, A.G., 1999. Aluminium/silicon interactions in conifers. *J. Inorg. Biochem.* 76, 89–98.
- Hu, A.Y., Che, J., Shao, J.F., Yokosho, K., Zhao, X.Q., Shen, R.F., Ma, J.F., 2017. Silicon accumulated in the shoots results in down-regulation of phosphorus transporter gene expression and decrease of phosphorus uptake in rice. *Plant Soil* 1–9.
- Huang, Z.T., Li, Y.F., Jiang, P.K., Chang, S.X., Song, Z.L., Liu, J., Zhou, G.M., 2014. Long-term intensive management increased carbon occluded in phytolith (PhytOC) in bamboo forest soils. *Sci. Rep.* 4, 3602.
- Huang, Y.T., Lowe, D.J., Churchman, G.J., Schipper, L.A., Cursons, R., Zhang, H., Chen, T.Y., Cooper, A., 2016. DNA adsorption by nanocrystalline allophane spherules and nanoaggregates, and implications for carbon sequestration in Andisols. *Appl. Clay Sci.* 120, 40–50.
- Jastrow, J.D., Amonette, J.E., Bailey, V.L., 2007. Mechanisms controlling soil carbon turnover and their potential application for enhancing carbon sequestration. *Clim. Chang.* 80, 5–23.
- Jobbágy, E.G., Jackson, R.B., 2000. The vertical distribution of soil organic carbon and its relation to climate and vegetation. *Ecol. Appl.* 10, 423–436.
- Jobbágy, E.G., Jackson, R.B., 2001. The distribution of soil nutrients with depth: global patterns and the imprint of plants. *Biogeochemistry* 53, 51–77.
- Jones, A.M., Collins, R.N., Rose, J., Waite, T.D., 2009. The effect of silica and natural organic matter on the Fe (II)-catalysed transformation and reactivity of Fe (III) minerals. *Geochim. Cosmochim. Ac.* 73, 4409–4422.
- Kaiser, K., Guggenberger, G., Haumaier, J., Zech, W., 1997. Dissolved organic matter sorption on subsoils and minerals studied by C-13-NMR and DRIFT spectroscopy. *Eur. J. Soil Sci.* 48, 301–310.
- Keiluweit, M., Bougoure, J.J., Nico, P.S., Pett-Ridge, J., Weber, P.K., Kleber, M., 2015. Mineral protection of soil carbon counteracted by root exudates. *Nat. Clim. Chang.* 5, 588–595.
- Kleber, M., Johnson, M.G., 2010. Advances in understanding the molecular structure of soil organic matter implications for interactions in the environment. *Adv. Agron.* 106, 77–142.
- Kleber, M., Nico, P.S., Plante, A., Filley, T., Kramer, M., Swanston, C., Sollins, P., 2011. Old and stable soil organic matter is not necessarily chemically recalcitrant: implications for modeling concepts and temperature sensitivity. *Glob. Chang. Biol.* 17, 1097–1107.
- Kleber, M., Eusterhues, K., Keiluweit, M., Mikutta, C., Mikutta, R., Nico, P.S., 2014. Mineral–organic associations: formation, properties, and relevance in soil environments. *Adv. Agron.* 130, 1–140.
- Konhauser, K.O., Ferris, F.G., 1996. Diversity of iron and silica precipitation by microbial mats in hydrothermal water, Iceland: implications for Precambrian iron formations. *Geology* 24, 323–326.
- Kostic, L., Nikolic, N., Bosnic, D., Samardzic, J., Nikolic, M., 2017. Silicon increases phosphorus (P) uptake by wheat under low P acid soil conditions. *Plant Soil* 419, 447–455.
- Lal, R., 2004a. Soil carbon sequestration impacts on global climate change and food security. *Science* 304, 1623–1627.
- Lal, R., 2004b. Soil carbon sequestration to mitigate climate change. *Geoderma* 123, 1–22.
- Lehmann, J., Kleber, M., 2015. The contentious nature of soil organic matter. *Nature* 528, 60–68.
- Lehmann, J., Solomon, D., Kinyangi, J., Dathe, L., Wirrick, S., Jacobsen, C., 2008. Spatial complexity of soil organic matter forms at nanometre scales. *Nat. Geosci.* 1, 238–242.
- Liang, Y.C., Wong, J.W.C., Wei, L., 2005. Silicon-mediated enhancement of cadmium tolerance in maize (*Zea mays* L.) grown in cadmium contaminated soil. *Chemosphere* 58, 475–483.
- Lima, M.D.R., Barros Jr., U.O., Barbosa, M.A.M., Segura, F.R., Silva, F.F., Batista, B.L., Lobato, A.K.S., 2016. Silicon mitigates oxidative stress and has positive effects in *Eucalyptus platyphylla* under aluminum toxicity. *Plant Soil Environ.* 62, 164–170.
- Liu, X.D., Lu, X.C., Wang, R.C., Zhou, H.Q., Xu, S.J., 2008. Surface complexes of acetate on edge surfaces of 2:1 type phyllosilicate: insights from density functional theory calculation. *Geochim. Cosmochim. Ac.* 72, 5896–5907.
- Loucaides, S., Behrends, T., Van Cappellen, P., 2010. Reactivity of biogenic silica: surface versus bulk charge density. *Geochim. Cosmochim. Ac.* 74, 517–530.
- Lucas, Y., 2001. The role of plants in controlling rates and products of weathering: importance of biological pumping. *Annu. Rev. Earth Pl. Sc.* 29, 135–163.
- Lucas, Y., Luizao, F.J., Chauvel, A., Rouiller, J., Nahon, D., 1993. The relation between biological activity of the rain forest and mineral composition of soils. *Science* 260, 521–523.
- Ma, J.F., Takahashi, E., 1990. Effect of silicon on the growth and phosphorus uptake of rice. *Plant Soil* 126, 115–119.
- Ma, J.F., Miyake, Y., Takahashi, E., 2001. Silicon as a beneficial element for crop plants. In: Datnoff, L.E., Snyder, G.H., Korndörfer, G.H. (Eds.), *Silicon in Agriculture. Studies in Plant Science Vol. 8*. Elsevier, Amsterdam, pp. 17–39.
- Ma, J.F., Tamai, K., Yamaji, N., Mitani, N., Konishi, S., Katsuhara, M., Ishiguro, M., Murata, Y., Yano, M., 2006. A silicon transporter in rice. *Nature* 440, 688–691.
- Machmuller, M.B., Kramer, M.G., Cyle, T.K., Hill, N., Hancock, D., Thompson, A., 2015. Emerging land use practices rapidly increase soil organic matter. *Nat. Commun.* 6, 6995.
- Maher, K., Chamberlain, C.P., 2014. Hydrologic regulation of chemical weathering and the geologic carbon cycle. *Science* 343, 1502–1504.
- Marxen, A., Klotzbücher, T., Jahn, R., Kaiser, K., Nguyen, V.S., Schmidt, A., Schädler, M., Vetterlein, D., 2016. Interaction between silicon cycling and straw decomposition in a silicon deficient rice production system. *Plant Soil* 398, 153–163.
- Masion, A., Vilge-Ritter, A., Rose, J., Stone, W.E.E., Teppen, B.J., Rybacki, D., Bottero, J.Y., 2000. Coagulation-flocculation of natural organic matter with Al salts: speciation and structure of the aggregates. *Environ. Sci. Technol.* 34, 3242–3246.
- Mataix-Solera, J., Cerdà, A., Arcenegui, V., Jordán, A., Zavala, L.M., 2011. Fire effects on soil aggregation: a review. *Earth-Sci. Rev.* 109, 44–60.
- Matichenkov, V.V., Bocharnikova, E.A., 2001. The relationship between silicon and soil physical and chemical properties. In: Datnoff, L.E., Snyder, G.H., Korndörfer, G.H. (Eds.), *Silicon in Agriculture. Studies in Plant Science Vol. 8*. Elsevier, Amsterdam, pp. 209–219.
- Matichenkov, V.V., Snyder, G.H., 1996. The mobile silicon compounds in some South Florida soils. *Eurasian Soil Sci.* 12, 1165–1180.
- Matus, F., Rumpel, C., Neculman, R., Panichini, M., Mora, M.L., 2014. Soil carbon storage and stabilisation in andic soils: a review. *Catena* 120, 102–110.
- Meunier, J.D., Colin, F., Alarcon, C., 1999. Biogenic silica storage in soils. *Geology* 27, 835–838.
- Meunier, J.D., Guntzer, F., Keller, S.K., 2008. Terrestrial plant-Si and environmental changes. *Mineral. Mag.* 72, 263–267.
- Mikutta, R., Mikutta, C., Kalbitz, K., Scheel, T., Kaiser, K., Jahn, R., 2007. Biodegradation of forest floor organic matter bound to minerals via different binding mechanisms. *Geochim. Cosmochim. Ac.* 71, 2569–2590.
- Mikutta, R., Schaumann, G.E., Gildemeister, D., Bonneville, S., Kramer, M.G., Chorover, J., Chadwick, O.A., Guggenberger, G., 2009. Biogeochemistry of mineral–organic associations across a long-term mineralogical soil gradient (0.3–4100 kyr), Hawaiian islands. *Geochim. Cosmochim. Ac.* 73, 2034–2060.
- Minasny, B., Malone, B.P., McBratney, A.B., Angers, D.A., Arrouays, D., Chambers, A., Chaplot, V., Chen, Z.-S., Cheng, K., Das, B.S., Field, D.J., Gimona, A., Hedley, C.B., Hong, S.Y., Mandal, B., Marchant, B.P., Martin, M., McConkey, B.G., Mulder, V.L., O'Rourke, S., Richer-de-Forges, A.C., Odeh, I., Padarian, J., Paustian, K., Pan, G., Poggio, L., Savin, I., Stolbovoy, V., Stockmann, U., Sulaeman, Y., Tsui, C.-C., Vågen, T.-G., van Wesemael, B., Winowiecki, L., 2017. Soil carbon 4 per mille. *Geoderma* 292, 59–86.
- Mizota, C., van Reeuwijk, L.P., 1989. Clay mineralogy and chemistry of soils formed in volcanic material in diverse climatic regions. In: *Soil Monograph 2*. ISRIC, Wageningen.
- Monger, H.C., Kelly, E.F., 2002. Silica minerals, Chap. 20. In: Dixon, J.B., Schulze, D.G. (Eds.), *Soil Mineralogy with Environmental Applications. Book Series SSSA No.7pp*. 611–636 Madison, WI.
- Moulton, K.L., Berner, R.A., 1998. Quantification of the effect of plants on weathering: studies in Iceland. *Geology* 26, 895–898.
- Moulton, K.L., West, J., Berner, R.A., 2000. Solute flux and mineral mass balance approaches to the quantification of plant effects on silicate weathering. *Am. J. Sci.* 300,

- 539–570.
- Oades, J.M., 1988. The retention of organic matter in soils. *Biogeochemistry* 5, 35–70.
- Oliva, P., Viers, J., Dupre, B., Fortune, J.P., Martin, F., Braun, J.J., Nahon, D., Robain, H., 1999. The effect of organic matter on chemical weathering: study of a small tropical watershed: Nsimi-Zoetele site, Cameroon. *Geochim. Cosmochim. Acta* 63, 4013–4035.
- Omoike, A., Chorover, J., 2004. Spectroscopic study of extracellular polymeric substances from *Bacillus subtilis*: aqueous chemistry and adsorption effects. *Biomacromolecules* 5, 1219–1230.
- O'Rourke, S.M., Angers, D.A., Holden, N.M., McBratney, A.B., 2015. Soil organic carbon across scales. *Glob. Chang. Biol.* 21, 3561–3574.
- Pan, W., Kan, J., Inamdar, S., Chen, C., Sparks, D., 2016. Dissimilatory microbial iron reduction release DOC (dissolved organic carbon) from carbon-ferrihydrite association. *Soil Biol. Biochem.* 103, 232–240.
- Parr, J.F., Sullivan, L.A., 2005. Soil carbon sequestration in phytoliths. *Soil Biol. Biochem.* 37, 117–124.
- Parr, J.F., Sullivan, L.A., 2014. Comparison of two methods for the isolation of phytolith occluded carbon from plant material. *Plant Soil* 374, 45–53.
- Parr, J.F., Sullivan, L.A., Chen, B., Ye, G., 2010. Carbon bio-sequestration within the phytoliths of economic bamboo species. *Glob. Chang. Biol.* 16, 2661–2667.
- Pedersen, H.D., Postma, D., Jakobsen, R., Larsen, O., 2005. Fast transformation of iron oxyhydroxides by the catalytic action of aqueous Fe(II). *Geochim. Cosmochim. Acta* 69, 3967–3977.
- Pei, Z.F., Ming, D.F., Liu, D., Wan, G.L., Geng, X.X., Gong, H.J., Zhou, W.J., 2010. Silicon improves the tolerance to water-deficit stress induced by polyethylene glycol in wheat (*Triticum aestivum* L.) seedlings. *J. Plant Growth Regul.* 29, 106–115.
- Piperno, D.R., 1988. *Phytolith Analysis: An Archaeological and Geological Perspective*. Academic Press, London.
- Piperno, D.R., 2016. Phytolith radiocarbon dating in archaeological and paleoecological research: a case study of phytoliths from modern neotropical plants and a review of the previous dating evidence. *J. Archaeol. Sci.* 68, 54–61.
- Pokrovski, G.S., Schott, J., Farges, F., Hazemann, J.L., 2003. Iron (III)-silica interactions in aqueous solution: insights from X-ray absorption fine structure spectroscopy. *Geochim. Cosmochim. Acta* 67, 3559–3573.
- Puppe, D., Ehrmann, O., Kaczorek, D., Wanner, M., Sommer, M., 2015. The protozoic Si pool in temperate forest ecosystems – quantification, abiotic controls and interactions with earthworms. *Geoderma* 243–244, 196–204.
- Rasmussen, C., Southard, R.J., Horwath, W.R., 2006. Mineral control of organic carbon mineralization in a range of temperate conifer forest soils. *Glob. Chang. Biol.* 12, 834–847.
- Reithmaier, G.M.S., Knorr, K.H., Arnold, S., Planer-Friedrich, B., Schaller, J., 2017. Enhanced silicon availability leads to increased methane production, nutrient and toxicant mobility in peatlands. *Sci. Rep.* 7, 8728.
- Reyerson, P.E., 2007. Terrestrial Silica Biogeochemical Cycles: Soil and Fluvial Fluxes.
- Reynolds, O.L., Keeping, M.G., Meyer, J.H., 2009. Silicon-augmented resistance of plants to herbivorous insects: a review. *Ann. Appl. Biol.* 155, 171–186.
- Rumpel, C., Kögel-Knabner, I., 2011. Deep soil organic matter—a key but poorly understood component of terrestrial C cycle. *Plant Soil* 338, 143–158.
- Rumpel, C., Chabbi, A., Marschner, B., 2012. Carbon storage and sequestration in subsoil horizons: knowledge, gaps and potentials. In: Lal, R., Lorenz, K., Hüttl, R.F., Schneider, B.W., von Braun, J. (Eds.), *Recarbonization of the biosphere: ecosystems and global carbon cycle*. Springer Science Business Media, pp. 445–464.
- Schmidt, M.W.I., Torn, M.S., Abiven, S., Dittmar, T., Guggenberger, G., Janssens, I.A., Kleber, M., Kögel-Knabner, I., Lehmann, J., Manning, D.A.C., Nannipieri, P., Rasse, D.P., Weiner, S., Trumbore, S.E., 2011. Persistence of soil organic matter as an ecosystem property. *Nature* 478, 49–56.
- Schulze, K., Borken, W., Muhr, J., Matzner, E., 2009. Stock, turnover time and accumulation of organic matter in bulk and density fractions of a Podzol soil. *Eur. J. Soil Sci.* 60, 567–577.
- Scott, E.E., Rothstein, D.E., 2014. The dynamic exchange of dissolved organic matter percolating through six diverse soils. *Soil Biol. Biochem.* 69, 83–92.
- Shoji, S., Nanzyo, M., Dahlgren, R.A., 1993. *Volcanic Ash Soils — Genesis, Properties and Utilization*. Elsevier, Amsterdam.
- Six, J., Conant, R.T.E., Paul, A., Paustian, K., 2002. Stabilization mechanisms of soil organic matter: implications for C-saturation of soils. *Plant Soil* 241, 155–176.
- Smetacek, V., Klaas, C., Strass, V.H., 2012. Deep carbon export from a Southern Ocean iron-fertilized diatom bloom. *Nature* 487, 313–319.
- Sollins, P., Kramer, M.G., Swanston, C., Lajtha, K., Filley, T., Aufdenkampe, A.K., Wagai, R., Bowden, R.D., 2009. Sequential density fractionation across soils of contrasting mineralogy: evidence for both microbial- and mineral controlled soil organic matter stabilization. *Biogeochemistry* 96, 209–231.
- Sommer, M., Kaczorek, D., Kuzyakov, Y., Breuer, J., 2006. Silicon pools and fluxes in soils and landscapes—a review. *J. Plant Nutr. Soil Sci.* 169, 310–329.
- Song, A., Ning, D., Fan, F., Li, Z., Provance-Bowley, M., Liang, Y., 2015. The potential for carbon bio-sequestration in China's paddy rice (*Oryza sativa* L.) as impacted by slag-based silicate fertilizer. *Sci. Rep.* 5, 17354.
- Song, Z.L., Zhao, S.L., Zhang, Y.Z., Hu, G.L., Cao, Z.H., Wong, M.H., 2011. Plant impact on CO₂ consumption by silicate weathering: the role of bamboo. *Bot. Rev.* 77, 208–213.
- Song, Z.L., Liu, H.Y., Si, Y., Yin, Y., 2012a. The production of phytoliths in China's grasslands: implications to biogeochemical sequestration of atmospheric CO₂. *Glob. Chang. Biol.* 18, 3647–3653.
- Song, Z.L., Wang, H.L., Strong, P.J., Li, Z.M., Jiang, P.K., 2012b. Plant impact on the coupled terrestrial biogeochemical cycles of silicon and carbon: implications for biogeochemical carbon sequestration. *Earth-Sci. Rev.* 155, 319–331.
- Song, Z.L., Liu, H.Y., Li, B.L., Yang, X.M., 2013. The production of phytolith-occluded carbon in China's forests: implications to biogeochemical carbon sequestration. *Glob. Chang. Biol.* 19, 2907–2915.
- Song, Z.L., Wang, H.L., Strong, P.J., Shan, S.D., 2014. Increase of available soil silicon by Si-rich manure for sustainable rice production. *Agron. Sustain. Dev.* 34, 813–819.
- Song, Z.L., McGrouther, K., Wang, H.L., 2016. Occurrence, turnover and carbon sequestration potential of phytoliths in terrestrial ecosystems. *Earth-Sci. Rev.* 158, 19–30.
- Street-Perrott, F.A., Barker, P.A., 2008. Biogenic silica: a neglected component of the coupled global continental biogeochemical cycles of carbon and silicon. *Earth Surf. Proc. Land.* 33, 1436–1457.
- Struyf, E., Conley, D.J., 2012. Emerging understanding of the ecosystem silica filter. *Biogeochemistry* 107, 9–18.
- Struyf, E., Smis, A., Van Damme, S., Garnier, J., Govers, G., Van Wesemael, B., Conley, D.J., Batelaan, O., Frot, E., Clymans, W., Vandevenne, F., Lancelot, C., Goos, P., Meire, P., 2010. Historical land use change has lowered terrestrial silica mobilization. *Nat. Commun.* 1, 129.
- Sulman, B.N., Phillips, R.P., Oishi, A.C., Shevliakova, E., Pacala, S.W., 2014. Microbe-driven turnover offsets mineral-mediated storage of soil carbon under elevated CO₂. *Nat. Clim. Chang.* 4, 1099–1102.
- Takahashi, T., Dahlgren, R.A., 2016. Nature, properties and function of aluminum-humus complexes in volcanic soils. *Geoderma* 263, 110–121.
- Taylor, L.L., Quirk, J., Thorley, R.M., Kharecha, P.A., Hansen, J., Ridgwell, A., Lomas, M.R., Banwart, S.A., Beerling, D.J., 2015. Enhanced weathering strategies for stabilizing climate and averting ocean acidification. *Nat. Clim. Chang.* 6, 402–406.
- Toma, Y., Clifton-Brown, J., Sugiyama, S., Nakaboh, M., Hatano, R., Fernández, F.G., Stewart, J.R., Nishiwaki, A., Yamada, T., 2013. Soil carbon stocks and carbon sequestration rates in seminatural grassland in Aso region, Kumamoto, southern Japan. *Glob. Chang. Biol.* 19, 1676–1687.
- Torn, M.S., Kleber, M., Zavaleta, E.S., Zhu, B., Field, C.B., Trumbore, S.E., 2013. A dual isotope approach to isolate carbon pools of different turnover times. *Biogeosciences* 10, 8067–8081.
- Trembath-Reichert, E., Wilson, J.P., McGlynn, S.E., Fischer, W.W., 2015. Four hundred million years of silica biomineralization in land plants. *P. Natl. Acad. Sci.* 112, 5449–5454.
- Turner, R.E., Rabalais, N.N., Justic, D., Dortch, Q., 2003. Global patterns of dissolved N, P and Si in large rivers. *Biogeochemistry* 64, 297–317.
- Turpault, M.P., Gobran, G.R., Bonnaud, P., 2007. Temporal variations of rhizosphere and bulk soil chemistry in a Douglas fir stand. *Geoderma* 137, 490–496.
- Umemura, M., Takenaka, C., 2014. Biological cycle of silicon in moso bamboo (*Phyllostachys pubescens*) forests in central Japan. *Ecol. Res.* 29, 501–510.
- Van Bockhaven, J., Spichal, L., Novák, O., Strnad, M., Asano, T., Shoshi Kikuchi, S., Höfte, M., De Vleeschauwer, D., 2015. Silicon induces resistance to the brown spot fungus *Coellobolus miyabeanus* by preventing the pathogen from hijacking the rice ethylene pathway. *New Phytol.* 206, 761–773.
- Vandevenne, F., Struyf, E., Clymans, W., Meire, P., 2012. Agricultural silica harvest: have humans created a new loop in the global silica cycle? *Front. Ecol. Environ.* 10, 243–248.
- von Lützow, M., Kögel-Knabner, I., Ekschmitt, K., Matzner, E., Guggenberger, G., Marschner, B., Flessa, H., 2006. Stabilization of organic matter in temperate soils: mechanisms and their relevance under different soil conditions - a review. *Eur. J. Soil Sci.* 57, 426–445.
- Wagai, R., Mayer, L.M., 2007. Sorptive stabilization of organic matter in soils by hydrous iron oxides. *Geochim. Cosmochim. Acta* 71, 25–35.
- Wagai, R., Mayer, L.M., Kitayama, K., Shirato, Y., 2013. Association of organic matter with iron and aluminum across a range of soils determined via selective dissolution techniques coupled with dissolved nitrogen analysis. *Biogeochemistry* 112, 95–109.
- Watteau, F., Villemain, G., 2001. Ultrastructural study of the biogeochemical cycle of silicon in the soil and litter of a temperate forest. *Eur. J. Soil Sci.* 53, 385–396.
- White, A.F., Blum, A.E., 1995. Effects of climate on chemical weathering in watersheds. *Geochim. Cosmochim. Acta* 59, 1729–1747.
- Whitmore, A.P., Kirk, G.J.D., Rawlins, B.G., 2015. Technologies for increasing carbon storage in soil to mitigate climate change. *Soil Use Manage.* 31, 62–71.
- Wiesmeier, M., Spörllein, P., Geuß, U., Hangen, E., Haug, S., Reischl, A., Schilling, B., von Lützow, M., Kögel-Knabner, I., 2012. Soil organic carbon stocks in southeast Germany (Bavaria) as affected by land use, soil type and sampling depth. *Glob. Chang. Biol.* 18, 2233–2245.
- Wilding, L.P., 1967. Radiocarbon dating of biogenic opal. *Science* 156, 66–67.
- Wüst, R.A.J., Bustin, R.M., 2003. Opaline and Al-Si phytoliths from a tropical mire system of West Malaysia: abundance, habit, elemental composition, preservation and significance. *Chem. Geol.* 200, 267–292.
- Ye, M., Song, Y., Long, J., Wang, R., Baerson, S.R., Pan, Z., Zhu-Salzman, K., Xie, J., Cai, K., Luo, S., Zeng, R., 2013. Priming of jasmonate-mediated antiherbivore defense responses in rice by silicon. *P. Natl. Acad. Sci.* 110, 3631–3639.
- Yin, J., Yang, X., Zheng, Y., 2014. Influence of increasing combustion temperature on the AMS ¹⁴C dating of modern crop phytoliths. *Sci. Rep.* 4, 6511.
- Yu, G., Ren, W., Chen, Z., Zhang, L., Wang, Q., Wen, X., He, N., Zhang, L., Fang, H., Zhu, X., Gao, Y., Sun, X., 2016. Construction and progress of Chinese terrestrial ecosystem carbon, nitrogen and water fluxes coordinated observation. *J. Geograph. Sci.* 26, 803–826.
- Yuan, G., Theng, B.K.G., Parfitt, R.L., Percival, H.J., 2000. Interactions of allophane with humic acid and cations. *Eur. J. Soil Sci.* 51, 35–41.
- Zhang, J.C., Zhang, L., Wang, P., Huang, Q.W., Yu, G.H., Li, D.C., Shen, Q.R., Ran, W., 2013. The role of non-crystalline Fe in the increase of SOC after long-term organic manure application to the red soil of southern China. *Eur. J. Soil Sci.* 64, 797–804.
- Zhang, X.D., Song, Z.L., McGrouther, K., Li, J.W., Li, Z.M., Ru, N., Wang, H.L., 2016. The impact of different forest types on phytolith-occluded carbon accumulation in sub-tropical forest soils. *J. Soils Sediments* 16, 461–466.
- Zhao, Q., Poulson, S.R., Obrist, D., Sumaila, S., Dynes, J.J., McBeth, J.M., Yang, Y., 2016. Iron-bound organic carbon in forest soils: quantification and characterization.

- Biogeosciences 13, 4777–4788.
- Zhao, Q., Adhikari, D., Huang, R., Patel, A., Wang, X., Tang, Y., Obrist, D., Roden, E.E., Yang, Y., 2017. Coupled dynamics of iron and iron-bound organic carbon in forest soils during anaerobic reduction. *Chem. Geol.* 464, 118–126.
- Zunino, H., Borie, F., Aguilera, S., Martin, J.P., Haider, K., 1982. Decomposition of ^{14}C -labeled glucose, plant and microbial products and phenols in volcanic ash-derived soils of Chile. *Soil Biol. Biochem.* 14, 37–43.
- Zuo, X., Lu, H., Zhang, J., Wang, C., Sun, G., Zheng, Y., 2016. Radiocarbon dating of prehistoric phytoliths: a preliminary study of archaeological sites in China. *Sci. Rep.* 6, 26769.
- Zuo, X., Lu, H., Jiang, L., Zhang, J., Yang, X., Huan, X., He, K., Wang, C., Wu, N., 2017. Dating rice remains through phytolith carbon-14 study reveals domestication at the beginning of the holocene. *Proc. Natl. Acad. Sci. U. S. A.* 114 (25), 6486.